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UNIVERSITY OF ALBERTA

Long Term Stability of Cellulosic Fibres: Effect of Alkaline Deacidifying Agents on Aged Cotton Fabrics.

BY

Esther Méthé

(C)

A Thesis

Submitted to the Faculty of Graduate Studies and Research

in Partial Fulfillment of the Requirements for the degree

of Master of Science

Department of Clothing and Textiles

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommended to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled LONG TERM STABILITY OF CELLULOSIC FIBRES: EFFECT OF DEACIDIFYING AGENTS ON AGED COTTON FABRICS submitted by ESTHER METHE in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in CLOTHING AND TEXTILES.

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Date: 21 June 1989

ABSTRACT

In spite of the protective effect that deacidifying agents are known to give to new or artificially aged cellulosic textiles [Kerr, 1982; Block, 1982; Jennings, 1984; Burgess, 1986], textile conservators wonder if these agents are safe to use on naturally aged cellulosic textiles. The long term effect of deacidifying agents: calcium hydroxide ($Ca(OH)_2$), magnesium bicarbonate, ($Mg(HCO)_2$, and methoxy magnesium methyl carbonate (Wei T'o® #2) was evaluated using three naturally aged and one artificially aged cotton fabrics. Randomly selected specimens of each fabric were treated with the deacidifying agents and distilled water, which was used as control. Accelerated aging was carried out in air at 100C, 100% RH for 15 days. Specimens of each fabric were examined before and after accelerated aging for physical and chemical changes: colour difference, pH of aqueous extracts, degree of polymerization, carbonyl and carboxyl content results. After accelerated aging deacidified naturally aged specimens showed smaller decreases in degree of polymerization than water-treated control specimens (35 to 50% versus 70%). Colour change (ΔE) was typically two to four NBS units less than the control cotton (16.27 versus 18.00). In all but one case, after accelerated aging the carbonyl content of deacidified specimens was lower than that of control cotton. Carboxyl content were inconsistent. Deacidified naturally aged specimens maintained a pH above 7.4 after accelerated aging while the aqueous extract pH of the water-treated control dropped to around 5. The results showed that the deacidifying agents did not damage the textiles, and slowed down degradation upon aging. The tests for colour, pH and degree of polymerization were efficient in assessing textile damage, while the carbonyl and carboxyl tests need to be re-evaluated. Correlation between pH and degree of polymerization demonstrated that pH is a useful indicator of chemical degradation of cotton. Further research on older textiles should be done.

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1. INTRODUCTION

1.1. Statement of the problem

Museum collections contain a large quantity of cellulosic textiles (i.e: cotton, linen, etc.). Garments and accessories, tapestries, carpets, and upholstery textiles, and painting canvasses are some of the forms celiulosic textiles can have. In spite of the fact that cellulosic textiles are fairly resistant to aging, textile conservators are concerned about their permanence. Various treatments received during their processing and use (eg: mercerization, bleaching, and cleaning), environmental conditions (eg: air pollution and storage), may affect the chemical structure of the fibres. The acidification of cellulosic textiles, and the ensuing degradative effects, are a major concern of conservators.

The pioneering research in conservation of cellulosic products was done on paper. Thus the conservation techniques which have been developed, such as deacidification treatments, were oriented towards paper products. Few studies [Peacock, 1980; Kerr, 1979, 1982; Block, 1981; Jennings, 1984; Burgess, 1986] have been done in relation to textiles. Some of the research examined both physical and chemical changes occurring in cotton textiles in relation to various deacidifying treatments [Block, 1981 Kerr, 1982; Burgess, 1986] while others focussed on physical changes [Peacock, 1980; Jennings, 1984]. While there is a consensus on the positive effects of deacidifying agents on new cellulosic textiles, their application on naturally aged textiles is controversial [Block, 1981; Kerr, 1982; Burgess, 1986]. More research with regards to the use of deacidifying agents on historic textiles has to be done in order to help textile conservators to select appropriate techniques to slow down the degradation of cellulosic textiles.

The aim of this research project is to determine whether naturally aged cotton textiles are chemically damaged by treatment with selected deacidifying agents.

1.2. Objectives

A. To determine whether there is change in the colour of naturally aged cotton textiles treated with deacidifying agents.

B. To determine whether there is a modification in the pH of aqueous extracts of naturally aged cotton textiles treated with deacidifying agents.

C. To determine whether there is a modification in the intrinsic viscosity and the degree of polymerization of naturally aged cotton textiles treated with deacidifying agents.

D. To determine whether there is a modification in the carbonyl content of naturally aged cotton textiles treated with deacidifying agents.

E. To determine whether there is a modification in the carboxyl content of naturally aged cotton textiles treated with deacidifying agents.

1.3. Null Hypotheses

1. There is no significant difference in the colour of naturally aged cotton after deacidification.
2. There is no significant difference in the pH of aqueous extracts of naturally aged cotton after deacidification.
3. There is no significant difference in the intrinsic viscosity and the degree of polymerization of naturally aged cotton after deacidification.
4. There is no significant difference in the carbonyl content of naturally aged cotton after deacidification.
5. There is no significant difference in the carboxyl content of naturally aged cotton after deacidification.

1.4. Limitations

1. The results of this research will be only applicable to cotton treated with the same deacidifying agents.
2. Due to the use of naturally aged cotton, there is no control on the type and level of oxidation initially present in the textile. This fact has to be taken into consideration when comparison is made with other studies.
3. The conditions used for accelerated aging are a compromise and may produce reactions that are different from those which occur during natural aging.

1.5. Definitions

Accessibility: "defines the ease by which the functional groups of the polymer molecule can be reached by the reactant molecules" [Segal, 1964, p.45].

Durability: expresses the degree to which a product retains its original qualities under continual usage [Browning, 1977, p.316].

Reactivity: "is the ability of the polymer chain molecule to react with other molecules" [Segal, 1964, p.45].

Permanence: "refers to the retention of significant use properties, particularly folding endurance and color, over a prolonged period" [Browning, 1977, p.316].

2. LITERATURE REVIEW

2.1. Cellulose

2.1.1. Fibre structure

Cotton is a natural fibre of vegetable origin. It is the seed hair produced by a variety of plant species belonging to the *gossypum* family [Cook, 1984]. Examination of the fibre reveals that it contains a cuticle, a primary wall, a secondary wall, and a lumen [see Figure 1].

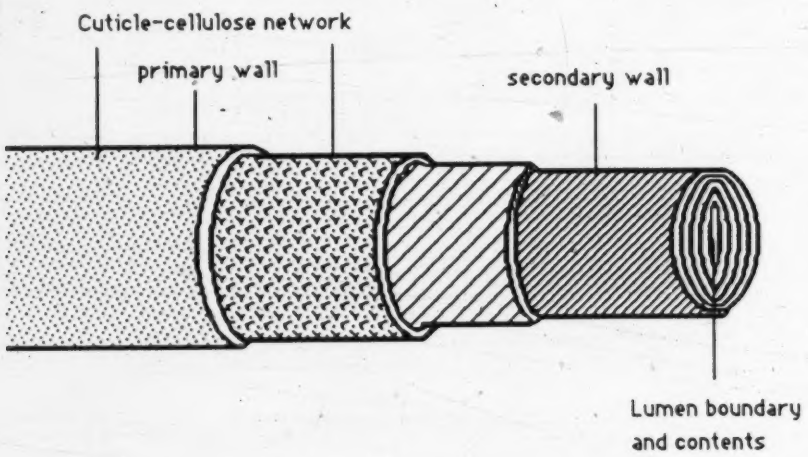

Figure 1. Morphological structure of the cotton fibre. [modified from Cook,1984]

The cuticle, a very thin layer which coats the primary wall, is composed of waxes, pectins, and protein materials [Segal and Wakelin, 1983]. The cuticle has the function of protecting the fiber [Peters, 1963].

The inner structure of the plant is a function of the growth which occurs in two phases. During the first phase, formation of the primary wall occurs. This primary wall is like a long tube with one extremity joined to the seed and the other end closed [Cook, 1984]. The primary wall acts as a fine shell of 0.1 to 0.2 μm thickness [Peters,

1963] containing the nutrients for the growing fibre. Pectin, wax and protein are part of the composition of the primary wall, as well as the cuticle; however, the primary wall also consists of approximately 50% cellulose [Nevell & Zeronian, 1985]. In the primary wall the cellulose is organized into microfibrils. Peters [1963, p.165] states that " the fibrils are laid down in such a way that those in the outside of the wall are mainly in a longitudinal direction to the fibre axis whereas those on the inside are transverse. Between these inner and outer layers, the fibrils are laid down in a spiral fashion probably making an angle of about 70º to the fibre axis" .

During the second phase of growth the secondary wall is laid down. It is formed by layers of cellulose deposited on the inner part of the primary wall. Since the growth occurs on the inside, it does not affect the diameter of the fibre. These layers of [Segal,1984] cellulose, which are referred as lamellae [Nevell & Zeronian, 1985] or rings [Peters, 1963], have a fibrillar structure. The final fibre structure proceeds by a stepwise grouping of structures of increasing size (molecules, micelles, microfibrils, fibrils and then fibre). In the first step, the molecules group together to form the micelles. These align themselves to form the microfibrils. Then the microfibrils align and orient themselves to form the fibrils. Finally, the fibrils are built up to form the fibre [Cook, 1984].

As in the primary wall, there is a particular organization of the fibrils in the secondary wall. The secondary fibrils are laid down spirally and form an angle with the fibre axis of approximately 20-30º. The spiral direction reverses periodically [Nevell and Zeronian, 1985; Cook, 1984]. The secondary wall is about 4 to 5 mμ thick and represents 90% of the total weight of the fibre [Peters, 1963]. However, according to Peters [1963] the formation, size and pattern of the rings or lamellae in cellulose fibres have been shown to be dependent on variations in light and temperature during the growing period.

The lumen is the cavity in the center of the fibre containing the liquid nutrients and protoplasm [Cook, 1984] as well as coloring matter [Peters, 1963]. The size of the lumen varies according to different factors such as moisture content, maturity, or finishing treatments like mercerization. The lumen represents approximately one third of the cross sectional area of an undried fibre. Once dried, this proportion is reduced to one twentieth or less of the fibre [Peters, 1963]. In a mature cotton fibre the secondary wall is well developed, thus decreasing the size of the hollow lumen. By consequence, the lumen in a dry mature fibre looks like a fine slit. An immature fibre does not contain as much cellulose as in the secondary wall. This underdevelopment leaves a large lumen which shows very distinctly in a cross section viewed under the microscope [Cook, 1984].

The length and the shape of the fibre varies according to species, growth conditions and maturity. A mature fibre after drying looks like a flat twisted ribbon, the twists reversing every two or three convolutions [Cook, 1984] and its cross-section has a kidney-bean shape [see Plate 1].

2.1.2. Molecular structure

2.1.2.1. Formation and conformation

Cellulose, which is the chief constituent of the cell walls of plants, is a carbohydrate with an empirical formula of $(C_6H_{10}O_5)_n$ [Guthrie, 1974]. It is a long chain polymer classified as a homopolysaccharide because the molecules are composed of a repeated unit called cellobiose. It is made of two ß-D-anhydroglucopyranose rings (frequently named anhydroglucose) [Nevell & Zeronian, 1985] [see Figure 2]. The ring originates from the reaction of the aldehyde group at C_1 and the hydroxyl group at C_5 of a molecule of D-glucose to form a hemiacetal linkage. The β-D-anhydroglucopyranose ring is one of the two possible stereoisomers (α or β) that may be formed at C_1 by D-glucose [see Figure 3] [Lehninger, 1982].

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Plate 1. Longitudinal and cross-section of a cotton fibre. [Shirley Institute, 1987]

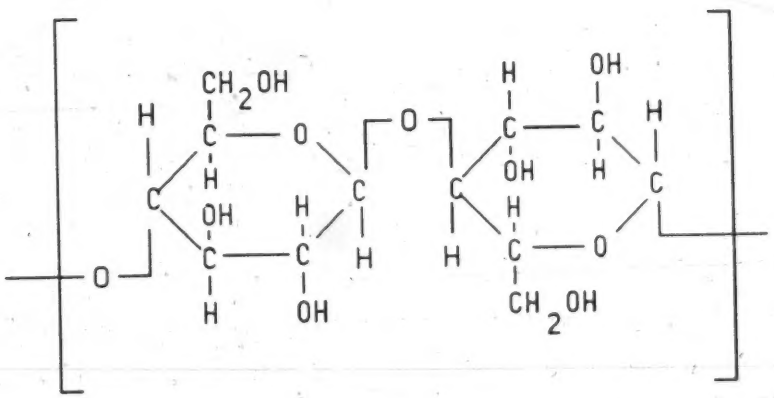


Figure 2. Cellobiose

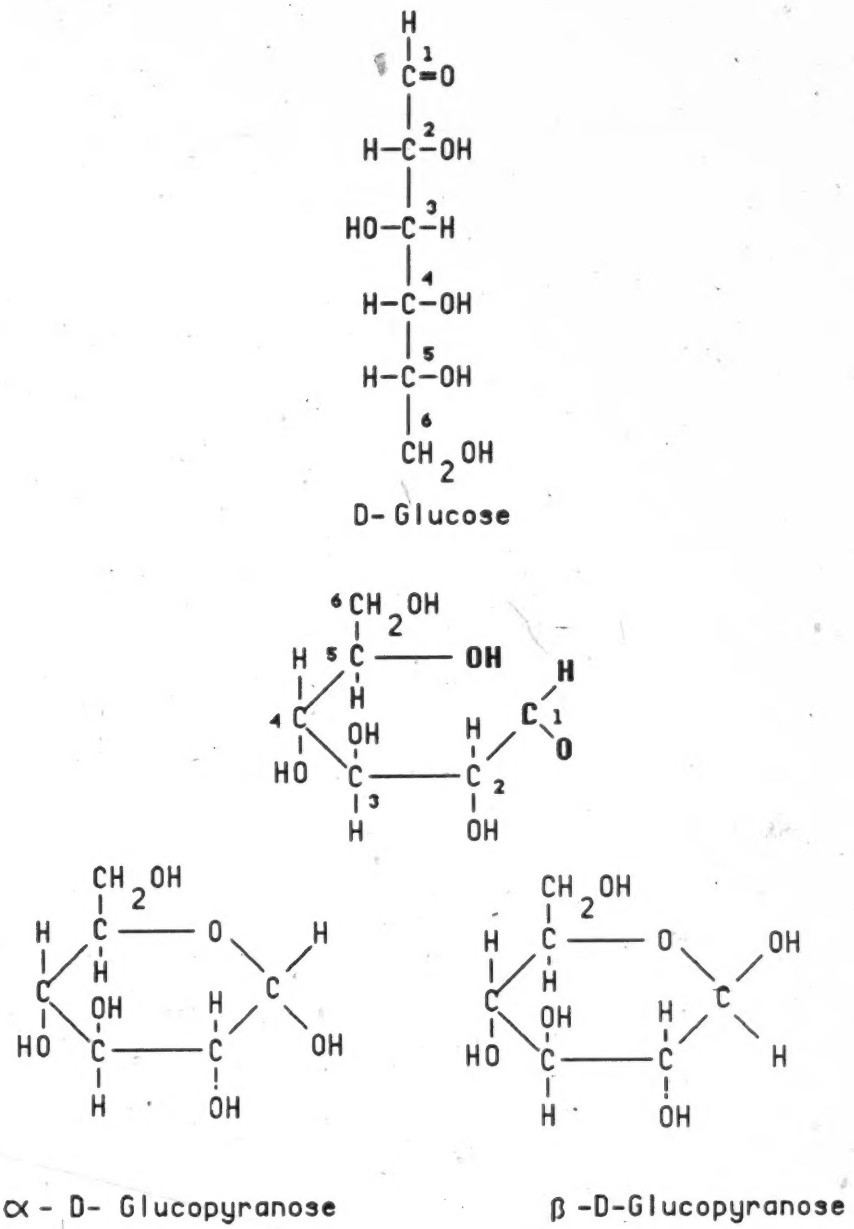


Figure 3. Formation of the two possible ring structures of D-glucopyranose. [Lehninger, 1982, p.282]

The two anhydroglucose molecules in cellobiose are joined together by a 1,4-β-glycosidic bond [Nevell and Zeronian, 1985]. This linkage results from a condensation reaction. It proceeds by the elimination of one molecule of water between hydroxyl groups attached to carbon 1 of one molecule of anhydroglucose unit and carbon 4 of another one [Segal, 1983] [see Figure 4]. The hydroxyl groups and the glycosidic bonds are equatorial with respect to the mean plane of the ring [Nevell and Zeronian, 1985; Guthrie, 1974] [see Figure 5].

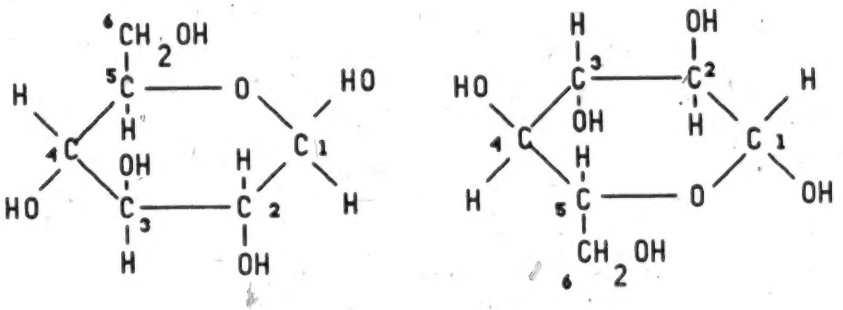
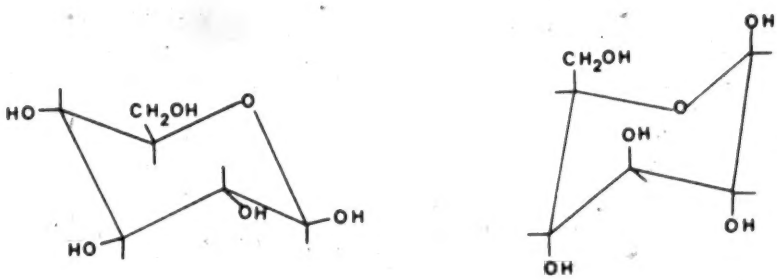


Figure 4. Two molecules of ß-D-glucose in position for elimination of one molecule of water. [Segal, 1983 p. 819.]



ß-D-Glucopyranose:
-OH and -CH_2OH groups are equatorial

ß-D-Glucopyranose:
-OH and -CH_2OH groups are axial

Figure 5. Stereochemistry of ß-D-glucopyranose rings.

2.1.2.2. Degree of polymerization

The degree of polymerization [DP] of cellulose, which is the number of anhydroglucose units per molecule, varies according to the source and condition of cellulose. When determined by ultracentrifugation, a typical DP of flax was evaluated at 36,000 , of cotton at 10,800, of sulphite pulp at 2,000 to 3,000, and of viscose rayon at 460 [Peters,1963, p. 186] [see Table 1]. The degree of polymerization calculated from viscosity-average molecular weight data is considerably lower. The D.P. is also influenced by treatments received and the level of degradation of the fibre. Change in the degree of polymerization is an important means of determining the reactivity of cellulose fibres towards various chemicals and the ability of the agents to degrade cellulose.

source	DP
flax	36,000
cotton	10,800
sulphite pulp	2-3,000
viscose rayon	460

Table 1. Degree of polymerization of cellulose in various products. [Peters, 1963, p.186].

2.1.2.3. Crystalline and amorphous regions.

Crystallinity in polymers such as cellulose "implies an intramolecular ordering as well as regularity in three dimensions" [Atalla, 1981, p.170]. The ordering and regularity in cellulose is achieved through hydrogen bonding and Van der Waals forces. The hydroxyl groups as well as the oxygen atoms in each ring and between adjacent rings are involved in inter and intra molecular hydrogen bonds. These hydrogen bonds combined with other secondary valence forces, such as Van der Waals forces, hold

together portions of the molecular chains into various degrees of lateral order. The molecules may be grouped into regions which vary in order from perfectly ordered crystal lattices to randomly ordered areas [Segal, 1971] Crystalline and amorphous regions are not sharply defined. One cellulose molecule is long enough that it can pass through several areas of varying order [Segal, 1971].

The crystalline regions are closely packed together, thus limiting access by reagents. However, the reduce number of hydrogen bonds among molecules in the amorphous regions make these regions more vulnerable to chemical attack. The proportion of crystalline or non-accessible regions and amorphous or accessible regions present in a fibre influences the cellulose properties [Cook, 1984] Cotton fibres in good condition are usually about 70% crystalline and 30% amorphous.

2.1.2.4. Fiber reactivity

The cellulose chain is made of three parts: the reducing (C_1) and non-reducing (C_4) end units, and the intermediate unit [see Figure 6]. The intermediate unit, inserted between the chain end units, is the main section of the chain. Due to the high degree of polymerization of cotton, this part has a major influence on the chemical reactivity of the fibre. To a lesser degree the chain end units contribute, each in its own way, to the reaction of the molecule. The end group on C_1 is a reducing end unit because it has an aldehyde group exposed in the form of a hemiacetal. This very important group is involved in specific reactions such as alkaline degradation (peeling reaction) once it has been oxidized to a carbonyl group. On C_4, a secondary hydroxyl reacts in the same way as other hydroxyl groups of this type.

The hydroxyl groups [OH], the ring oxygen of the anhydroglucose ring and the glycosidic bond are the strategic points involved in the chemical reactivity of cellulose. The hydroxyl groups are usually the most reactive parts; they can be oxidized, esterified or converted into ether linkages. There are two secondary alcohols, one on C_2 and one on

C_3, and one primary alcohol on C_6. These alcohols have different reactivities which are determined by their type and position, and by the reagents used.

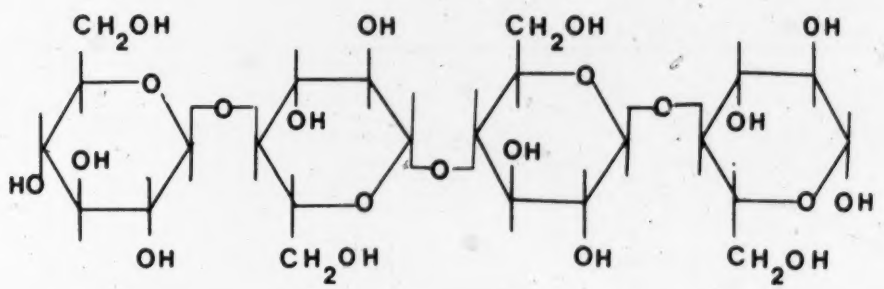


Figure 6. The three parts of the cellulose chain. [Peters, 1963, p. 181].

2.2. Chemical reactions

The two main chemical reactions involved in cellulose degradation are oxidation and hydrolysis. The severity and the rate of the reactions are dependant on the concentration and the strength of the reagents, the temperature and the presence of catalysts.

2.2.1. Oxidation

2.2.1.1. Points of oxidation

Under oxidative conditions, cellulose produces oxycellulose. Two types of oxycellulose can be formed according to the kind of oxidizing agent used and the pH of the reaction medium [Segal, 1983]. Under acidic and neutral conditions an oxycellulose of high reducing capacity, characterized by the presence of carbonyl groups, is produced. An alkaline solution produces an acidic oxycellulose which is recognized by the presence of carboxyl groups [Rutherford & Harris, 1943] [see Table 2]. Naturally aged cellulosic fabrics are likely to contain both reducing and acidic oxycellulose.

pH	Groups per scission		
	COOH	CHO	CO
5	1.1	3.6	4.8
6	1.2	3.55	4.4
7	1.3	3.4	3.6
8	2.0	3.0	2.6
9	3.4	1.9	0.65
10	5.0	0.8	0.0

Table 2. Dependence on pH of the number of functional groups formed during the hypochlorite oxidation of cellulose
[T. P. Nevell, 1985, p. 259]

The rate of oxidation is influenced by pH, temperature, concentration of oxidant, and nature of the oxidizing reagent [Rutherford & Harris, 1943,]. The rate of oxidation may also be influenced by the presence in the system of a third substance acting as a catalyst, such as reduced vat dye or metallic ions such as iron or copper [Rutherford & Harris, 1943; Ward, 1964].

Narkar [1974, p. 42] enumerates the theoretically possible modes of oxidation [see Figure 7]:

1. Attack at carbon atoms C_2 or C_3 or both to produce >C=O groups without fission of the carbon-carbon bond giving an acyloin or diketone.
2. Oxidation of the 2, 3 dihydroxy groups to aldehyde H-C=O resulting in carbon-carbon bond fission and the formation of dialdehyde.
3. Further oxidation of these aldehydic groups to carboxyl groups.
4. Partial further oxidation of aldehydic groups produced by (2) to produce one carboxyl group and leave one aldehydic group.
5. Oxidation of the primary hydroxyl group on C_6 to an aldehydic group.

6. Oxidation of the primary hydroxyl group on C_6 to the carboxyl group depending upon the conditions of oxidation.
7. The terminal hydroxyl group on C_4 could be oxidized to a ketone group or the ring may be ruptured simultaneously at 2:3 and 3:4 positions with the resultant formation of dialdehyde and formic acid. The aldehyde may be further oxidized to the dicarboxylic acid.
8. The hemiacetal end-groups may be oxidized to carboxyl groups.

These attacks result in a reducing oxycellulose for reactions 1, 2, and 5, an acidic oxycellulose for the reactions 3, 6 , and 8, and cellulose of both reducing power and acidic character for reactions 4 and 7.

Nevell [1985] gives three reasons to explain the complexity of the cellulose oxidation. These are:

1. The three alcohol groups in each chain unit react differently.
2. Different parts of cellulose have different accessibilities.
3. Various oxidants behave in different ways.

The first two reasons, concerning the different reactivities of hydroxyl groups and the accessibility of the amorphous regions over the crystalline regions, have already been reviewed in Section 2.1.2. entitled "Molecular Structure". The third reason presents a new aspect which concerns elements external to the molecule: the oxidizing agents. Certain oxidants are considered specific oxidants (e.g. periodate) in which one reaction is favored, while other oxidants result in a non-specific oxidation in which oxidation at various hydroxyl groups can occur simultaneously [Nevell, 1985].

The differences between the oxycelluloses are of major importance because different types of oxycellulose vary in their sensitivities towards chemicals. It is essential to consider these differences when a treatment such as deacidification is to be applied to aged textiles.

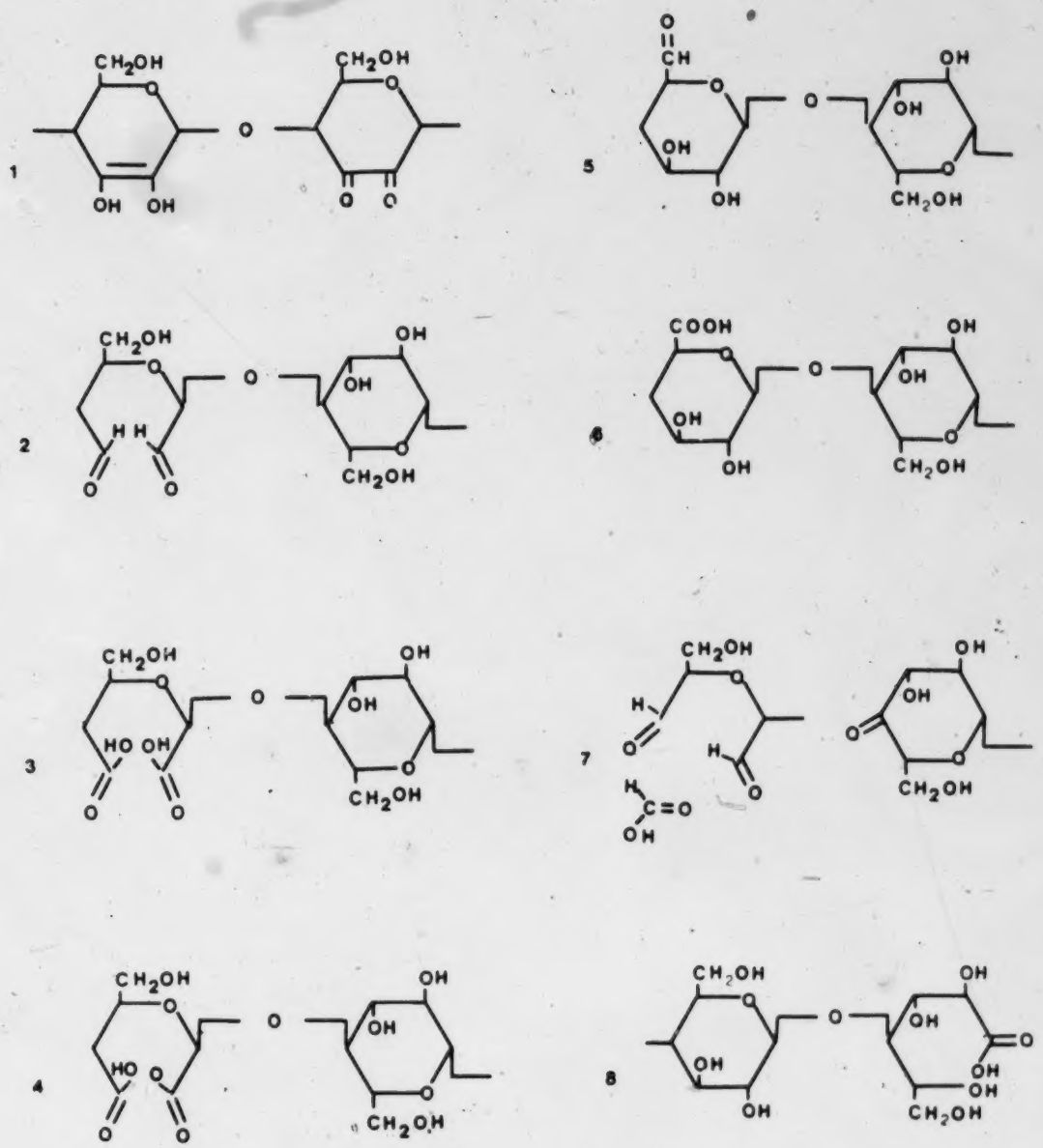


Figure 7. Types of oxidation according to Narkar.

2.2.1.2. Sources of oxidation

The sources of oxidation for cellulosic fabrics are multiple. Some are inherent to the textile processing such as bleaching; others are a consequence of textile use such as light, heat, or cleaning treatment. The oxidation proceeds in different ways according to the source.

Bleaching: Sodium chlorite, sodium hypochlorite and hydrogen peroxide are the most common oxidizing agents used in bleaching treatments of cotton. Each possesses inherent characteristics which make it suitable for a specific purpose.

Sodium hypochlorite is a non-specific oxidant. Its action upon cellulose depends on the pH at which the treatment is done. In an acidic medium, sodium hypochlorite gives a reducing type of oxycellulose while in an alkaline medium, in which the oxidant is mainly the hypochlorite ion, it gives an acidic oxycellulose. At a pH between 5 and 8.5 the predominance of hypochlorous acid in the solution accelerates the rate of the oxidation and increases the risk of damage to a textile. Thus the control of pH during a treatment is important to prevent weakening of the fibres. Bleaching is usually done at a pH greater than 10 [Trotman, 1984]. According to the pH of the bleach bath the chemical reaction is the following:

(a) $NaOCl \longrightarrow Na^+ + OCl^-$

(b) $HOCl \longrightarrow H^+ + OCl^-$

(c) $HOCl + H^+ + Cl^- \longrightarrow Cl_2 + H_2O$

Reaction (a) which predominates at pH 10. Reaction (b) predominates at pH 5 to 8.5. Below pH 5 the liberation of chlorine begins and at pH 3, hydrochlorous acid is converted to chlorine [K. Dickinson,1986, p.73].

Hydrogen peroxide is commercially used for bleaching protein and cellulose fibres. Its use is also recommended in textile conservation treatment when bleaching is required [Landi, S, 1985; Burgess, 1980]. Hydrogen peroxide acts as a weak acid.

$$H_2O_2 \rightleftharpoons H^+ + HO_2^-$$

$$\frac{[H^+] + [HO_2^-]}{[H_2O_2]} = K \qquad K = 1.78 \times 10^{-12}$$

K = dissociation constant

Undissociated forms of hydrogen peroxide are rather stable. Since in acidic solution it is mainly undissociated, commercial preparations are usually acidified.

The bleaching action of this peroxide results from the combination of activation and stabilization of its solution. During activation there is dissociation and formation of the perhydroxyl ion (OH_2^-), which is the active species of the bleaching process [Cegarra and Gacén, 1983]. The role of the stabilization is to optimize the bleaching process by avoiding formation of a useless by product such as molecular oxygen.

$$2HO_2^- \longrightarrow 2HO^- + O_2$$

Activation is accomplished in one of three ways: by the addition of alkalies, transformation into derivatives of higher activity (organic and inorganic peracids and by catalytic means with heavy metals ions (Cu, Fe) or enzymes [Cegarra and Gacén, 1983]. Only alkaline activation and catalytisis with heavy metals are of concern to this discussion.

The equilibrium of the dissociation reaction is displaced toward the right when alkali is added to an aqueous solution of hydrogen peroxide. This has the effect of favouring the formation of perhydroxyl ions (OH_2^-):

$$H_2O_2 + HO^- \longrightarrow H_2O + HO_2^-$$

However, due to the instability of the perhydroxyl ions , a stabilizer has to be used to minimize the formation of molecular oxygen:

$$2HO_2^- \longrightarrow HO^- + O_2$$

Heavy metal activation should be avoided in the presence of cotton since it enhances chemical degradation of the fibres.

According to some authors [Dickinson, 1986; Narkar 1974], the oxidation of cotton with hydrogen peroxide is characterized by ketone groups with very low aldehyde and carboxyl content. Narkar [1974] suggests that " The ketones formed are *inactive* carbonyls, i.e. do not cause the peeling off reaction and consequently almost no yellowing of cotton on ageing and on hot alkaline extraction is found." Nevell [1986] reports, however, that oxidation by alkaline peroxide almost certainly involves peroxy radicals and leads to the formation of carboxyl groups and a small proportion of reducing groups.

Sodium chlorite bleaching differs from sodium hypochlorite and hydrogen peroxide bleaching as the bleaching is done under acidic conditions. A pH of 4 is considered the most suitable for bleaching of cotton Dickinson [1986] indicated that the following reactions occur:

(a) $5ClO_2^- + 2H^+ \longrightarrow 4ClO_2 + Cl^- + 2HO^-$

(b) $4ClO_2 + 4H^+ \longrightarrow 3ClO_2 + 1/2\ Cl_2 + 2H_2O$

(c) $3ClO_2 \longrightarrow 2ClO_3^- + Cl^-$

When sodium chlorite is acidified two competing reactions, represented by (a) and (b), produce chlorine dioxide, the oxidizing agent. Some decomposition of ClO_2 to give chlorate and chloride ions also takes place (equation c) [K. Dickinson, 1986].

Scouring: In order to remove fats, waxes and other non-cellulosic constituents cotton is heated for several hours at atmospheric pressure at 100C or under elevated pressure at 125 to 130C with a dilute (2%) solution of sodium hydroxide. This process, known as scouring, is sometimes combined with desizing and/ or bleaching [Trotman, 1984; Dickinson, 1986].

Light: Light consists of electromagnetic radiation of varying energy. Ultraviolet and infrared waves are of greatest concern in the preservation of cellulosic textiles. Infrared radiation causes molecular vibration and drying of cellulosic fibres, whereas ultraviolet light causes bond scission. The mechanism of light damage, referred to as a

photochemical reaction, is related to the wave length of the energy. Photochemical reactions are of two types: photolysis and photosensitization. The first one is considered as a true photochemical reaction because the ultraviolet radiation has sufficient energy to break molecular bonds, shorten polymer chains and weaken fibres [Tucker et al., 1980].

The second type, photosensitization, is a secondary photochemical reaction. Photosensitization caused by visible light is of main interest here because cellulosic fibres are more likely to be damaged in this way than by photolysis. Impurities such as certain dyestuffs, finishes, soil, and contaminants present in the fabric act as photosensitizers. They "absorb light energy and transfer it to the oxygen in the surrounding atmosphere. Activated oxygen is produced, which may react to form hydrogen peroxide in the presence of water vapor. Both the activated oxygen and H_2O_2 may cause degradation of textiles by oxidation" [Morris & Wilsey, 1952]. Photosensitization of cellulose is dependent on the intensity of light, temperature, relative humidity (photodegradation increasing with a rise of relative humidity), air pollutants, and the type of dye and mordant used.

A distinction between damage from light and from other sources can sometimes be identified by looking at the pattern or the location of damaged areas; only the parts exposed to light are affected.

Heat and H_2O: In the presence of oxygen at moderate temperatures and over short periods of time cellulosic textiles are stable to heat . However, as the time of exposure to heat and the temperature increase, degradation of cellulose occurs through physical and chemical modificatıcns, including oxidation of the hydroxide groups. Zeronian [1985] observed that temperatures of 190C to 240C over 6 hours are sufficient to produce colour change which is indicative of oxidative damage.

According to Shafizadeh [1986] "the chemical reactions at temperatures up to 300C include reduction of the degree of polymerization (DP) by bond scission, appearance of

free radicals, elimination of water, formation of carbonyl, carboxyl, and hydroperoxide groups (especially in air), evolution of carbon monoxide and carbon dioxide, and finally production of a charred residue which can undergo further elimination, rearrangement and condensation reactions"

Thermal degradation at low temperatures is accelerated in the presence of air and water. Previous research comparing heating under oxygen and nitrogen has determined that at low temperatures oxygen is determinant in the oxidative process while at high temperatures it is not significant. Agreement on the temperature at which modifications of cellulose appear is not consistent among authors. Rutherford & Harris [1943] indicate that below 140C only a few changes occur. Kilzer [1971, p.1015] reported that "at above about 120C the thermal instability of cellulose and any of its derivatives becomes increasingly apparent... At temperatures only slightly above ambient (such as occur during processing and use), fabrics, fibreboard, tire cord, and the like experience heat-accelerated loss of desirable properties. " Farquhar subjected cotton to temperatures from 50C to 200C for 4 to 24 hours in air and nitrogen. She reported that "oxidative action began at lower temperatures and accelerated thermal decomposition at higher temperatures" [Farquhar,1956, p.55].

Autocatalytic oxidation can also occur by the formation of carboxylic acid groups and carbon dioxide. This process can be important in sealed containers in which volatile decomposition products are retained [Shafizadeh, 1985].

2.2.2. Hydrolysis

By definition hydrolysis may be presented as the acid catalyzed decomposition of a molecule accompanied by the addition of water [Lehninger, 1982]. In cellulose, hydrolysis occurs by cleavage at one or more glycosidic linkages and the product is called hydrocellulose. The reaction occurs in three stages (see Figure 8): "rapid protonation of the glysocidic oxygen atom, slow transfer of the positive charge to C_1 with consequent

formation of a carbonium ion and fission of the glycosidic bond, and rapid attack on the carbonium ion by water to give the free sugar residue and to re-form the hydroxonium ion " [Nevell, 1985]. The cleavage products at each point of scission are a reducing end unit at C_1 or a non-reducing end unit at C_4 as shown in Figure 9.

The hydrolysis can be more or less severe; in proportion to its severity, a decrease in chain length (DP) and tensile strength are observed. In theory, total hydrolysis results in conversion of cellulose to carbon dioxide and water [Peters, 1963], however, this end point is rarely seen. Usually a "levelling off" degree of polymerization of about 200 occurs after extensive hydrolysis.

Different hypotheses have been given to explain the sensitivity to hydrolysis of certain linkages over others. Nevell [1985] reviews and classifies possible causes into three categories. The first two categories are related to chemical structures. A link which is sensitive to hydrolysis may occur if an aldehyde or carboxyl group is near the glycosidic oxygen. This approach was studied by Sharples [1971], who presents a summary of the effect of chemical structure on hydrolysis. The second category concerns the "presence of a few sugar units other than anhydroglucose in the cellulose chain" [Nevell, 1985]. Authors do not agree on the exact nature of these sugars in cellulose; it is, however, believed that these sugars are not present in pure cellulose. The third category involves physical properties. This cause is explained by the presence of abnormal physical stresses at a few localized points while the fibers are being formed [Nevell, 1985]. Once again, there is no unanimity among the authors for the exact cause and sequence of these weaker points.

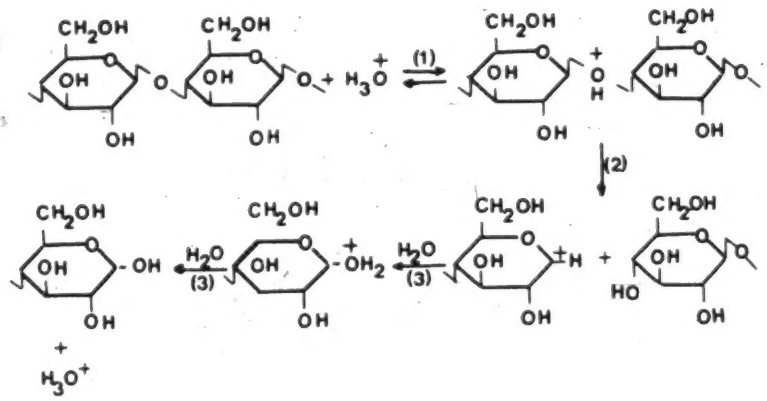


Figure 8. Hydrolysis: mechanism. [Nevell, 1985, p. 224]

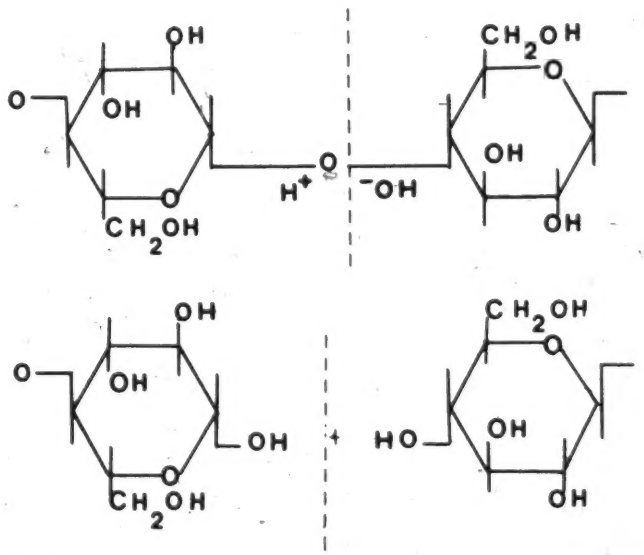


Figure 9. Hydrolysis: reducing unit at C_1 and non-reducing unit at C_4. [Nevell, 1985, p. 263]

2.2.3. Acid

2.2.3.1. Sources

At each phase of their life, through processing, use and storage, cellulosic textiles are exposed to various sources of acidic contaminants. Processes such as bleaching and dyeing can leave an acidic residue in the textiles. Air pollution, a consequence of industrialization and urbanization, provides undesirable environmental conditions. Sulphur dioxide and oxides of nitrogen which can respectively be oxidized to sulfuric and nitric acid are harmful to cellulosic products. Soils such as fresh perspiration and food stains of acidic character are other sources of damage. While in storage cellulosic textile can suffer from attack by volatile acids from unfinished wood and paper products.

2.2.3.2. Effect of acids on cellulose

Acids are the main agents inducing the hydrolysis of cellulose molecules. The effect is dependent on the strength and the concentration of the acid, as well as exposure time and temperature. The presence of agents such as iron can also influence the reaction by their catalytic character.

2.2.4. Alkali

2.2.4.1. Sources

The action of alkaline reagents on cellulosic textiles will receive special attention in this literature review because one objective of the research is to examine the effect of selected alkalies on oxidized cellulose.

The main exposure to alkali for cellulosic textiles is during processing: mercerization, and as mentioned in section 2.2.1.2., scouring and sometimes bleaching when carried out in alkaline medium. The information found in the literature about processing and cleaning methods refers mainly to present day techniques. Considering the problem from the point of view of a conservator, it is important to realize that all historic textiles did not necessarily follow the same steps. The processing and cleaning

treatments of cotton have been modified through time. Another source of exposure to an alkaline treatment in conservation is deacidification. Paper and textile conservators may choose to deacidify objects as a curative or preventive treatment.

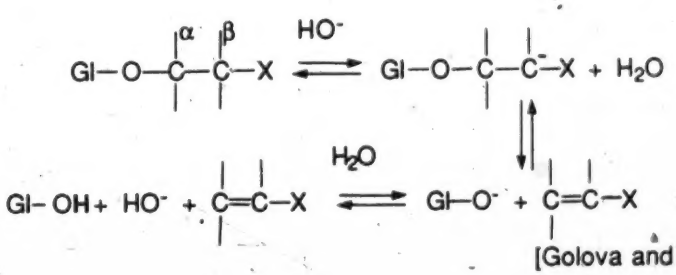
Mercerization: The origin of mercerization dates from the mid nineteenth century. It ensued from the observation of swelling of cotton and modification of certain of its properties by concentrated caustic soda [Valko, 1943]. Mercerization is now an important process in cotton textile production because it has the advantages of increasing the reactivity of cotton with other finishes as well as the tensile strength, absorbency, luster and . The actual process consists of swelling cellulose fibres with aqueous sodium hydroxide (18-27%). Mercerization does not modify the chemical composition of cellulose but alters the fibre morphology. The differences in properties observed between native (unmercerized) and mercerized cellulose are produced by an increase in molecular orientation and a decrease in crystallinity, hence an increase in amorphous regions. The greater reactivity of mercerized cellulose compared to native cellulose is dependant on the increased accessibility of the functional groups. This difference depends upon the way the mercerized cotton is dried (with or without tension) after treatment [Zeronian,1985].

Deacidifying agents: The purpose of the deacidifying agents used in conservation is to neutralize the acidity of cellulosic artefacts and prevent, by leaving an alkaline residue, further degradation. The application of the treatment itself is not necessarily done under alkaline conditions. The pH of the solution varies according to the product used. However, deacidification involves the deposition of an alkaline salt. Because of the differences between each deacidifying technique, it is important to distinguish between the advantages and disadvantages of each. Section 2.3 is devoted to deacidifying agents and a brief review of their use on textiles.

2.2.4.2. Effects of alkali on cellulose

Cellulose in good condition is not sensitive to alkalies. However, the introduction of carbonyl groups upon oxidation modifies the reactivity of cellulose. The fact that oxidized cellulose is sensitive to alkalies is very important to consider when working with historic textiles. Through their use, old textiles have been exposed to various sources of oxidation (light, air pollutant, bleaching...). Because much is unknown about the specific history of these naturally aged textiles, it is important to know the possible reactions of various types of oxycellulose toward alkali. This information will help to determine whether there is a safe temperatures and pH for alkaline products which might be involved in treatment of various types of oxidized cellulosic textiles.

Degradation of cellulose from the reducing end: It is reported that cellulose treated with alkali at temperatures up to 150C-170C suffers from loss of weight but not from considerable change in the degree of polymerization [Golova & Nosova, 1973; Zeronian, 1985]. This type of degradation is known as the "peeling" reaction. The reaction proceeds by a successive detachment of reducing units from the end of a cellulose chain. The process of the elimination is explained by Isbell [1944] in his theory of ß-elimination. This theory is based on the "instability towards alkalies of glycosides of alcohols containing electronegative groups in the ß-positions" [Golova & Nosova, 1973, p. 327].



XII

[Golova and Nosova, 1973]

This reaction, slow in native cotton, is much faster in oxycellulose and hydrocellulose. In oxidized cellulose ß-elimination can occur adjacent to any carbonyl groups which have been introduced in the molecule by oxidation (see Figure 10).

In order to stabilize the oxidized cellulose, the carbonyl groups can be reduced to hydroxyl groups or further oxidized to carboxyl groups [Nevell, 1985]. After hydrolysis of cellulose there are an increased number of reducing end-groups. As the number of reducing units increases, the possibility for the peeling reaction to occur increases.

The stopping reactions: The peeling reaction does not go to completion. It ends before the cellulose chain is totally consumed due to oxidation of the terminal reducing groups into non-reducing units containing carboxyl groups [Golova & Nosova, 1973].

Alkaline hydrolysis of glycosidic bonds: When cellulose is heated, at 170C and above, in an alkaline solution a rapid decrease of the degree of polymerization and loss of weight is observed. This reaction is due to the hydrolysis of the cellulose at the glycosidic links under the action of hydroxide ions [Golova & Nosova, 1973]. As in acidic conditions, alkaline hydrolysis of the chain forms new reducing end-groups, which are susceptible to the peeling reaction.

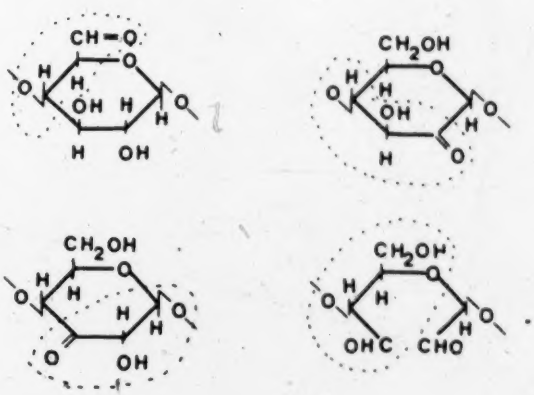


Figure 10:. ß-alkoxycarbonyl Groups in Carbonyl-Containing Oxidized Cellulose. [Richards, 1971, p. 1013]

2.3 Deacidifying agents for paper and cellulosic textiles

2.3.1. History

The degradation of relatively new books has motivated researchers to investigate the permanence of paper in order to find causes and remedies for this problem. The study of paper has shown that permanence is mainly determined by its components [Smith, 1970]. Paper produced prior to 1650 is often observed to still be in good condition, while paper from the beginning of the twentieth century had already suffered from degradation [Flieder, 1975].

The study of variations in methods of fabrication of paper helps to explain the modification in behavior of books from different time periods. Until the middle of the seventeenth century, paper was made of white rags. As the need for paper increased, coloured rags started to be used for the production. Various methods were tested in order to bleach these rags but it was only with the discovery of the properties of chlorine in 1774 that a method judged satisfactory was adopted. Unfortunately, the effects of the chlorine residues, which break down and give rise to hydrochloric acid, were ignored [Langwell, 1977]. During the nineteenth century, wood pulp gradually replaced the rags in paper production. Wood is more readily available as a source of cellulose but has the disadvantage of containing impurities such as lignin, hemicellulose and pectin. In order to obtain a white product, bleaching, with its consequences, is required. Moreover, paper made from wood pulp has to be sized to obtained a product appropriate for writing. Among the different types of size which were tried, the alum rosin size has been the most widely used. Unfortunately, this size has the inconvenient effect of leaving the paper acidic and thus contributing to its degradation.

The observation of the mechanism of cellulose degradation has shown that, in order to stabilize paper, the acidity present in paper has to be controlled. Moreover, old papers containing alkali reserve have demonstrated a greater stability over the years. Research in paper conservation has been oriented towards the control of the acidity in

paper and thus, the focus of this research has been the creation of deacidifying products. The effects of these products on paper vary from getting rid of acidity present in the paper to assuring prevention from further acidification by leaving an alkaline reserve in the paper. Three types have been developed: aqueous, non-aqueous (solvent) and vapor. Each type possesses advantages and disadvantages which have to be considered in relation to the type and condition of the document being treated.

There are no ideal deacidifying methods. A method has to be chosen in accord with the condition and the characteristic of the treated object as well as the time and budget allowed for the treatment. Deacidification processes do not provide a miracle solution. Cunha [1972, p. 203] summarizes the limitations of deacidifying treatment: "It does not decrease the probability of biological attack, because some fungi thrive in alkaline conditions. Nor does deacidification prevent oxidative decay or photo-chemical reaction, although alkaline buffering agents will neutralize any acid by-products of such attacks. Deacidifying will not strengthen paper already embrittled by acid-hydrolysis". However deacidification treatment slows down the process of degradation. In order to be successful, deacidification treatments should be inexpensive, easy to apply, and safe both for people and cellulosic products.

2.3.2 Methods of deacidification

In 1936, Schierholtz patented a technique which consisted of immersing paper in or spraying it with an aqueous solution of barium, calcium, or strontium bicarbonate or hydroxide [Kathpalia, 1973].

Barrow applied the principle of Schierholtz's work in his research on paper deacidification. The first application that he developed was a two-step technique. The treatment consists of immersing a document for 20 minutes in two solutions. The first immersion is done in a 0.15% solution of calcium hydroxide ($Ca(OH)_2$) [pH 12.5]. This solution neutralizes the acids present in the document. When the excess of calcium

hydroxide has been removed, the second immersion is done in a 0.15% calcium bicarbonate ($Ca(HCO_3)_2$) [pH 6.2]. This step converts the calcium hydroxide to calcium carbonate [Kathtalia, 1973]. The pH of the paper treated with this two step method is about 7.5 to 9.0 [Barrow Restoration Shop, 1976].

$$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O \qquad \text{XIII}$$

$$Ca(OH)_2 + Ca(HCO_3)_2 \longrightarrow 2CaCO_3 + 2H_2O \qquad \text{XIV}$$

[Cunha et al, 1972]

According to the W.J. Barrow Restoration Shop [1976, p. 161], "The calcium carbonate acts as a stabilizer against aging degradation and as a buffer against any acidic environment".

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + CO_2 + H_2O \qquad \text{XV}$$

[Cunha et al, 1972]

A simplified method, consisting in a one step technique, has been developed and is explained by Hey [1976].

There are some concerns from conservators that the calcium hydroxide method may degrade the cellulose due to the pH of 12.5 of the initial solution [Barrow Restoration Shop, 1976]. Hey rejects this idea, explaining that calcium hydroxide as well as barium hydroxide "does not possess the swelling/dissolving properties of the caustic alkali sodium hydroxide and does not damage the cellulose during its immersion period. In addition calcium ions are rapidly absorbed onto the cellulose and once the paper is removed from the solution at the end of the deacidification carbon dioxide is rapidly absorbed from the air so that the pH drops as conversion into the carbonate takes place" [Hey, 1976, p 75].

In the fifties, magnesium bicarbonate ($Mg(HCO_3)_2$) was used first by Gear at the United States National Archives and then by Barrow. The magnesium bicarbonate ($Mg(HCO_3)_2$) is prepared by adding magnesium carbonate ($MgCO_3$)to water into which carbon dioxide is bubbled .

$$MgCO_3 + CO_2 + H_2O \longrightarrow Mg(HCO_3)_2 \qquad \text{XVI}$$

[Cunha, 1972]

The technique for deacidification consists of soaking the documents for 20 to 30 minutes in the solution of magnesium bicarbonate which neutralizes the acids present. When drying, the unstable magnesium bicarbonate reverts to magnesium carbonate and carbon dioxide is released [Kathpalia, 1974].

$$Mg(HCO_3)_2 + H_2SO_4 \longrightarrow MgSO_4 + 2H_2O + 2CO_2 \qquad \text{XVII}$$

$$Mg(HCO_3)_2 + CO_2(air) \longrightarrow MgCO_3 + 2CO_2 + H_2O \qquad \text{XVIII}$$

$$MgCO_3 + H_2SO_4 \longrightarrow MgSO_4 + CO_2 + H_2O \qquad \text{XIX}$$

[Cunha et al, 1972]

Cunha et al [1972, p. 207] considered that the advantage of this method is to "revitalize paper in addition to deacidification because in the soaking process the cellulose fibers are relaxed and refibrillated and on drying the re-entanglement of the fibrils plus the renewed surface tension between the fiber surfaces often results in measurable increase in strength". This affirmation needs to be studied. In their research on the effect of $Mg(HCO_3)_2$ solutions on various paper, Wilson and associates [1981] concluded that reflectance, tear and tensile strength energy absorption increased with deacidification. However the sizing of the paper was destroyed and deacidification did not remove completely aluminium from carboxyl groups.

A version of this method was also prepared for spraying application. Spraying is judged less effective because the magnesium bicarbonate does not penetrate the fibres as well as in the immersion process [Kathpalia, 1973]. Kathpalia found that spraying causes cockling in document paper and does not impart as high a degree of stability. However, compared to the immersion technique, it has the advantage of being faster and thus more economical.

Two main disadvantages of the aqueous method are reported by Cunha et al [1972]. The first one is the risk encountered when a document has a special sensitivity towards water due to the presence of water soluble ink. The second is related to the cost and the time involved in the treatment because in order to be treated a book has to be dissassembled and then rebound.

In the 1950's, Langwell proposed a type of non-aqueous process which consisted of a solution of magnesium acetate in methanol. This product, releasing acetic acid, is considered too hazardous for cellulosic products [Smith, 1981].

At the British Museum Laboratory, Baynes-Cope used barium hydroxide in methyl alcohol for deacidification of documents sensitive to water. The solution is applied to the document by brushing, spraying or immersion [Kathpalia, 1973]. Barium hydroxide ($Ba(OH)_2$) first neutralizes the acid present. In the presence of carbon dioxide (CO_2) in the air the barium hydroxide is converted into barium carbonate ($BaCO_3$). The barium carbonate remains in the document and acts as a buffer against future contamination [Cunha, 1972].

$$Ba(OH)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2H_20 \qquad \text{XX}$$

$$Ba(OH)_2 + CO_2 \longrightarrow BaCO_3 + H_20 \qquad \text{XXI}$$

$$BaCO_3 + H_2SO_4 \longrightarrow BaSO_4 + CO_2 + H_20 \qquad \text{XXII}$$

[Cunha, 1972]

The toxicity of barium compounds and both toxicity and flammability of methanol are cited by many authors [Bayne-Cope, 1969; Cunha, 1972; Kathpalia, 1973; Kelly,

1976; Williams,1981]. Kelly [1972, p. 99] also reports that "the barium hydroxide imparts a pH of 13 to the paper which is certainly high enough to be detrimental. Hey's objection [1976] to the level of alkalinity, as seen previously, is also applicable to barium hydroxide.

Smith [1970] developed another non-aqueous process in the 1960's using a solution of magnesium methoxide ($(CH_3O)_2Mg$) in methanol. The magnesium methoxide is made by introducing magnesium metal into methyl alcohol.

$$Mg^{++} + 2CH_3OH \longrightarrow (CH_3O)_2Mg + 2H^+ \quad \textbf{XXIII}$$

[Cunha, 1972]

Once the solution of magnesium methoxide in methanol is applied to the paper, in a first step it reacts with the water contained in the paper to form magnesium hydroxide, which is a moderately strong alkali.

$$Mg(CH_3O)_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2CH_3OH \quad \textbf{XXIV}$$

[Cunha, 1972]

Kelly [1976] considers this phase hazardous because it exposes the paper to a strong alkali which can cause degradation of the cellulose. However no information on pH is provided. In the second step the magnesium hydroxide reacts with the acid present and converts it into a harmless magnesium salt and water.

$$Mg(OH)_2 + H_2SO_4 \longrightarrow MgSO_4 + 2H_2O \quad \textbf{XXV}$$

$$Mg(CH_3O)_2 + H_2SO_4 \longrightarrow MgSO_4 + 2(CH_3OH) \quad \textbf{XXVI}$$

[Cunha, 1972]

The excess of magnesium hydroxide, by exposure to carbon dioxide in the air, is converted into magnesium carbonate.

$$Mg(OH)_2 + 2CO_2 \longrightarrow MgCO_3 + CO_2 + H_2O \quad \textbf{XXVII}$$

[Cunha, 1972]

The magnesium carbonate will remain in the paper to neutralize any acid which may be introduced into the paper later on.

$$MgCO_3 + H_2SO_4 \longrightarrow MgSO_4 + CO_2 + H_2O \quad \textbf{XXVIII}$$

[Cunha, 1972]

The main problem of the process is the sensitivity of magnesium methoxide to water [Baynes-Cope, 1969; Cunha, 1972; Kathpalia, 1973; Kelly, 1976]. Any traces of moisture cause an early hydrolysis of the magnesium methoxide and its precipitation as magnesium hydroxide, insoluble in water and organic solvents, before penetrating the paper [Kelly, 1976]. Moreover, methyl alcohol has the inconvenience of being toxic and flammable product. In order to improve this product, the solution of magnesium methoxide was tried in a mixture of methyl alcohol and trichlorotrifluoroethane. The latter compound is neither toxic nor flammable.. This solvent has also the advantage of carrying the methoxide into the fibers without gelling [Cunha, 1973].

Non-aqueous methods are interesting because they are often safe for water sensitive products. Unfortunately, they do not provide entire satisfaction because they do not wash away soluble acid present in cellulose [Cunha, 1972; Santucci, 1974] and some inks are soluble in methyl alcohol [Kathpalia,1973].

The previous methods, both aqueous and non-aqueous, have the inconvenience of being too time consuming to be applicable to mass deacidification. Vapor phase deacidification provides a new approach to the problem.

In the 1960's, Langwell developed a method using cyclohexylamine carbonate (CHC). The cyclohexylamine carbonate is absorbed on sheets of paper which are, as treatment, subsequently placed in a book. The treatment proceeds as the vapor is released from the sheet and penetrates the books. The cyclohexylamine carbonate can also be used in powder form. It can be enclosed in paper envelopes and placed in sealed paper boxes [Langwell, 1966]. Kathpalia reports [1973, p.119] that according to the Barrow Research Laboratory "treatment with cyclohexylamine carbonate provides adequate deacidification and prolongs the retention of acceptable physical properties of acidic and non-acidic paper". However, the treatment is suspected to cause the destruction of rosin sizing, decreased brightness and yellowing of acidic paper. Cunha considers the cyclohexylamine carbonate as mildly effective in neutralization of acid in paper. The concentration is not judged strong enough to neutralize strong acids such as sulfuric acid. However, it is specified that "in closed books CHC is an effective, fairly long lasting interim measure until permanent deacidification with buffering can be accomplished" [Cunha, 1972, p.204-205]. Cyclohexylamine carbonate is considered to be a health hazard causing irritation of skin and the respiratory system [Kathpalia, 1973; Smith, 1981; Williams, 1981].

Kathpalia [1973] has been using a method based on ammonia. Documents and books which need to be deacidified are exposed to dilute ammonia (1:10) in a sealed chamber. A pH of 6.8 to 7.2 is obtained. This method was tested by Barrow and found to be inefficient. The treated papers were not stable and reverted to acidic condition within a short period of time.

The last two deacidification processes (CHC and ammonia) are considered by Smith as not being safe for paper as "cellulose and its derivatives can brown when exposed to amines, and ammonium sulfates and nitrate" [Smith, 1981, p. 417].

A vapor method based on morpholine was tried by Walker [1977]. The method proceeds by impregnation of whole books with a mixture of morpholine and water vapor.

After treatment the pH of the book stabilizes at about 6.3 to 6.7 and after accelerated aging at about 6.0. The advantages of this method are its low cost (in spite of the initial investment of $30,000 for equipment) and time saving. It has, however, the inconvenience of not working equally well on every paper.

A new process by Smith is being used at the Public Archives of Canada in Ottawa. It is a mass deacidification method using magnesium alkoxides and alkoxy carbonates in Freon 12 and methyl alcohol [Smith, 1981]. Another study for mass deacidification process is in progress at the Library of Congress. This method, developed by Kelly, involves the use of diethyl zinc (Et_2Zn). The process is described by Williams [1981, p. 219]. : "Books are first thoroughly dried under high vacuum, then diethyl zinc is introduced into the chamber. Three days are required for the gas to penetrate the closed books and to react with the cellulose. After the reaction is complete, the unused diethyl zinc is distilled off and saved. Carbon dioxide gas and water are introduced to convert the zinc cellulosate to zinc carbonate. The final pH is around 8. Two percent zinc carbonate is left in the paper as a reserve." This method needs special care because diethyl zinc is pyrophoric.

2.3.3. Proposed mechanisms of protection

It has been established that magnesium salts have a protective effect upon degradation of cellulose by oxygen in an alkaline medium [Robert et al, 1968]. As a result of this discovery, magnesium has been used in the paper industry as a way to stabilize the cellulose during alkaline bleaching. Other metal ions such as calcium and barium were tested; however, magnesium appeared to be the most efficient at inhibiting the degradation of cellulose [Defaye & Gadelle, 1976].

The mechanisms of the reaction are not well understood, and different hypotheses have been suggested as a result of research on the subject.

1. Considering that the degradation is related to the decomposition of peroxide, Croon and Andrew [1971] suggested that "the magnesium salts complex with peroxides formed in the reaction medium" [Defaye & Gadelle, 1974].

2. Ericsson et al [1971], starting from the thought that transition metals have a catalytic action upon the oxidative degradation of cellulose, proposed that "the magnesium salts act on transition metals present in the reaction medium." [Defaye & Gadelle, 1974].

3. Defay and Gadelle, without rejecting the previous hypothesis, suggested that the mechanism proceeds by " la chélation par le métal d'unités hexulopyranosidiques de la cellulose, dès le stade primaire d'oxidation, inhibant ainsi le transfert de charge aboutissant à l'élimination du substituant en ß de la fonction carbonyle ainsi créée. [Defay & Gadelle, 1976]. [see Figure 11].

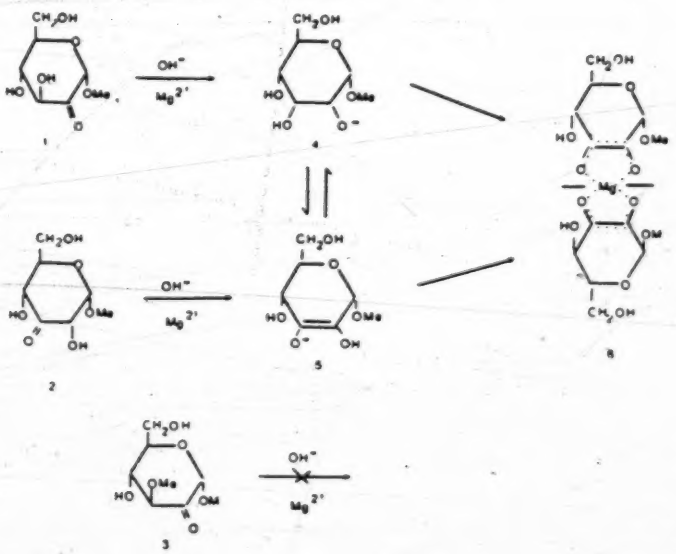


Figure 11. Defay and Gadelle, through NMR analysis, propose a complex between two molecules of hexuloside and one magnesium ion.This structure implies that carbon -2 and -3 of each ring are in the enediol form.
(1) methyl α-D-arabino - hexopyranosid-2-ulose
(2) methyl α-D-ribo-hexopyranosid-3-ulose.
[Kerr, 1982, p. 40].

2.3.4. Application to textiles

The use of deacidifying agents has not yet gained the same favor in textile conservation as it has in paper conservation. In the literature, there are only a few references to the application of deacidifying agents to textiles.

In 1980, Peacock tested deacidification of linen with water, magnesium carbonate, and methoxy magnesium methyl carbonate (Wei T'o ® #2). The products were applied, in both spray and immersion form, on an artificially aged linen. After an accelerated aging, the linen was tested for weight, pH, colour change, tensile strength, and stiffness. She found that deacidification decreases the rate of weight loss, acidification and strength loss, increases the stiffness and causes minimal colour change. Immersion application of aqueous treatments and spray application of non-aqueous treatment provided the best protection during accelerated heat aging.

Kerr [1982] studied alkaline buffers on cotton fabric. Her objectives were to determine whether alkaline buffers reduce the rate of degradation of the fabric during exposure to heat and humidity, to find which product out of the three tested would be the best to use in textile conservation, and to study the mode of degradation of alkaline buffered cotton. For her study, she applied calcium hydroxide, magnesium bicarbonate and methoxy magnesium methyl carbonate (Wei T'o ® #2) on cotton specimens and subjected them to accelerated aging. The textiles were tested for physical and chemical properties. In her conclusions Kerr reports that cotton fabric treated with alkaline buffered $Ca(OH_2)$, $Mg(HCO_3)_2$ or methoxy magnesium methyl carbonate deteriorated at a slower rate during accelerated aging than when unbuffered. Of all the buffers that she used the methoxy magnesium methyl carbonate was the most effective.

In 1984, Jennings studied the effect of deacidifying agents on new and naturally aged cotton fabrics. After treatment with methoxy magnesium methyl carbonate(both dipping, Wei T'o® #2, and spraying, Wei T'o® #12, formulae) and magnesium bicarbonate, she tested the pH and the following physical changes: colour change,

stiffness, moisture regain, and abrasion resistance. In her conclusion, she underlines the loss of resistance to flexing and abrading and mentions the importance of finding a way to reduce the stiffness of the fabrics after treatment with Wei T'o® dipping formula.

Block [1982] investigated the effect of an alkaline rinse on the aging of new and aged cellulosic textiles. Due to the physical and chemical modification occurring in the cellulose molecule, he is not in favour of the use of deacidifying agents on naturally aged textiles [Block, 1982]. A study conducted by Burgess [1986] supports this idea of a difference in reaction after accelerated aging between new and old fabrics. After an investigation of the effect of water washing on the long term stability of cellulosic fibers, Burgess concludes that "it is unlikely that alkaline solutions could pose any problems with new materials. But evidence indicates that, in certain situations, the long term stability of older fibers would be impaired". She explained the poor performance that she obtained for the fibres treated with calcium bicarbonate by the great increase in sensitivity towards alkali of naturally aged fibres [Burgess, 1986].

Some recommendations, with regard to the application of deacidifying agents to textiles, can be formulated from these studies. The application of deacidifying agents successfully reduces the rate of deterioration during artificial aging [Peacock,1980; Kerr,1982]. The selection of deacidifying agents should be done with regard to the characteristics of the treated textiles [Kerr, 1982; Jennings, 1984; Burgess 1986]. Further research on naturally aged textiles should be done [Block,1982; Jennings, 1984; Burgess, 1986].

3. MATERIALS AND METHODS

The uncertainty about the aging process and, consequently, the lack of knowledge about the chemical transformations which have occurred in historic cellulosic textiles, make textile conservators reluctant to use treatments such as deacidification. In this study, in order to overcome that problem, naturally aged cottons have been used to determine the possible effects of deacidifying agents on oxidized cellulose. Along with to the naturally aged fabrics, an artificially aged cotton was also tested, thereby allowing comparisons between both types of fabric.

3.1. Fabrics

The naturally aged fabrics were used in this study were white, plain weave bed sheets varying in age between 20 to 30 years [see Appendix I]. They had a yarn count (warp x weft)of 41 x 38 yarns/cm for A, 41 x 39 yarns/cm for B, and 74 x 67 yarns/cm for C. Each fabric was individually washed in a 0.2% Shurgain® anionic detergent solution, rinsed in distilled water and laid flat on a table to air dry. The artificially aged fabric was an unbleached plain weave cotton (Testfabrics 400U) having a yarn count of 34 x 32 yarns/cm. The artificial aging was done by bleaching for 30 minutes in a pH 7 hypochlorite solution prepared according to Burgess [1979]. More information about the bleaching process is available in Appendix II.

3.2 Sampling procedure

The cotton fabrics used in this experiment were not evenly aged. Chemical degradation caused by agents such as air pollutants, light, contact with acidic surfaces, cleaning and bleaching treatments had developed according to the use of the textile, therefore, damage was sometimes concentrated in specific areas. In order to minimize differences in

specimens, the sampling of each textile was done avoiding the use of too degraded areas such as yellowed or visibly weakened areas [see Appendix III].

From each fabric about 60 specimens were cut, none of them within 10 cm of the selvedges. The size of the specimens varied for each fabric: 15 x 25 cm for A and C, 15 x 25 cm for B, and 15 x 15 cm for D. Each specimen was numbered and assigned at random to the one of four treatments.

3.3 Application of alkaline buffers

Wei T'o® solution # 2 (methoxy magnesium methyl carbonate, MMMC)

The Wei T'o® solution # 2 is a solution of methoxy magnesium methyl carbonate, in methyl alcohol and trichlorotrifluoroethane available from Wei T'o Associates[1].

In order to avoid precipitation onto the fabric, prior to treatment all samples were dried in a vacuum oven at 55C for 7 hours and then stored in a desiccator. The Wei T'o® solution # 2 treatment consisted of a ten second dipping in the solution followed by a ten second draining. The samples were then dried flat on a plastic covered table.

Magnesium bicarbonate ($Mg(HCO_3)_2$) and Calcium Hydroxide ($Ca(OH)_2$)

For both treatments, the samples were immersed for 30 minutes at room temperature in a bath containing one of the solutions. Following immersion, they were drained 15 seconds and laid to dry flat on a plastic covered table.

The magnesium bicarbonate solution ($Mg(HCO_3)_2$) was prepared according to Wilson (1979). To a three litre beaker containing 2 litres of distilled water dry ice was added with stirring until a continuous flow of CO_2 had been generated. After a few minutes, 5.8 g of magnesium hydroxide was added. In order to maintain a continuous flow of gas , dry ice was added from time to time. After the undissolved magnesium bicarbonate was

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[1] Wei T'o Associates, P.O. Drawer 40, 21750 Main Street Unit 27, Matteson, Il 60443.

allowed to settle, the solution was decanted to a clean container and used immediately. The solution had an initial pH of 6.4.

The calcium hydroxide ($Ca(OH)_2$) was prepared according to Kerr [1982] by stirring 4 g of reagent grade calcium hydroxide ($Ca(OH)_2$) in 2 litres of distilled water for 2 minutes. The liquid was allowed to settle at room temperature for 24 hours. The clear solution was decanted into a clean container and used at once. The initial pH of the solution was of 11.7.

3.4. Accelerated aging procedure

Interpretation of chemical and physical changes occurring during accelerated aging is difficult. Most research on the effect of heat on cellulose is confined to changes occurring at temperatures of 170C or above [Shafizadeh, 1985; Zeronian, 1985; Kilzer, 1971]. Unfortunately, the observations resulting from these studies are not always applicable to experiments conducted at lower temperatures. Ernhardt et al [1987], after observing that "major reactions taking place at 150C hardly occur at lower temperatures", recommended that experimental work be conducted at lower temperatures and humidities in order to reproduce more accurately those changes which might occur during natural aging. In addition, Block [1984] recommends that accelerated aging of cellulosic material should not exceed 160C in either dry or humid conditions.

The samples were aged by heating them in air at a temperature of 100C and a relative humidity of 100%. The aging chamber consisted of a glass bath filled with oil and maintained at constant temperature using a Haake circulator model E3. Each fabric sample was rolled around a glass rod and inserted in a pressure test tube (Ace Glass, inc.)to which 1ml of distilled water had been previously added. The roll was suspended above the surface of water (between 1.5 to 3cm) in order to prevent direct contact with water. Once the pressure test tubes were capped with plastic lined caps, the glass tubes

were immersed in the oil bath for a period of 15 days. During the aging process, the test tubes were regularly inspected in order to detect any problems. The bath was covered with opaque material to exclude light. The tubes which were leaking air were taken out of the bath, quickly recapped, and replaced in the oil bath [see Appendix IV].

3.5. Test methods

3.5.1. Aqueous-extract pH

The aqueous extract pH was determined according to Tappi T509 OS-77 using a Fisher Accumet 230 pH meter. One gram of fabric cut into 5 x 5 mm squares was immersed for 1.5 hours in 70 ml distilled water. A pH measurement of the water was then taken making sure that the electrode did not touch the fabric. Two replicates were done for each treated fabric.

3.5.2. Colour change

The colour change of the fabric was determined immediately after deacidification and after 15 days of accelerated aging. Each serie of readings was done on ten specimens which were all layered together and oriented with the warp in the same direction. A Hunterlab Tristimulus Colorimeter Model D25M-9 was used to measure colour difference (ΔE) in the CIE $L^*a^*b^*$ scale (CIELAB) where L^*, a^*, and b^* describe respectively lightness, redness-greenness, yellowness-blueness. The total colour difference (ΔE) between fabrics having undergone different treatments was calculated as follows:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

where $\Delta L^* = L^*_{smp} - L^*_{std}$ (if $+\Delta L^*$, sample is lighter than standard
if $-\Delta L^*$, sample is darker than standard)

$\Delta a^* = a^*_{smp} - a^*_{std}$ (if $+\Delta a^*$, sample is redder than standard
if $-\Delta a^*$, sample is greener than standard)

$\Delta b^* = b^*_{smp} - b^*_{std}$ (if $+\Delta b^*$, sample is yellower than standard

if -Δb*, sample is bluer than standard)

[Hunter Associates Laboratory]

The standard on which colour difference after treatment and after aging was based was the L*, a*, and b* value of each specimen before treatment with deacidifying agents.

3.5.3. Degree of polymerization

Cadoxen, the common name for tris (ethylenediamine) cadmium dihydroxide ([Cd $(H_2NCH_2CH_2NH_2)_3](OH)_2$), was used as a solvent for the viscometric degree of polymerization of the cotton specimens. Although other solvents, such as cupriethylenediamine hydroxide solution (cuen) [ASTM method: D1795-62 reapproved 1985] and cuprammonium hydroxide solution (cuam) have been widely used, cadoxen is now in favour for several reasons. Cadoxen has the advantage of being colourless, transparent, odourless, and quite stable at room temperature [Jayme and Lang, 1963] Moreover, cellulose-cadoxen solutions have very good stability in the presence of oxygen [Jayme, 1971].

Cadoxen is a strong base which dissolves cellulose by overcoming in the crystalline areas forces, such as hydrogen bonds, which are holding together the fiber structure [Segal & Wakelin, 1983]. Once the intermolecular bonds are broken the solvent, through the metal ion cadmium, forms a coordinated complex with the celiulose. Cuam and cuen also form a coordinated complex with cellulose. Johnson [1985] explains the process using cuen as example; he states "The glycol group of a 1,4 anhydroglucose unit chelates to occupy two of the coordination sites of the copper ion, displacing a mole of ethylenediamine" [Johnson,1985, p. 183] [see figure 12]. According to Jayme [1971] optical rotational measurements made in studies of the reaction between cadoxen and glucopyranosides appears to confirm this idea. Because cadoxen solutions of cellulose

showing negative specific rotation a cellulose-cadoxen complex, involving the C_2 and C_3 hydroxy groups of the glucose units was assumed to formed.

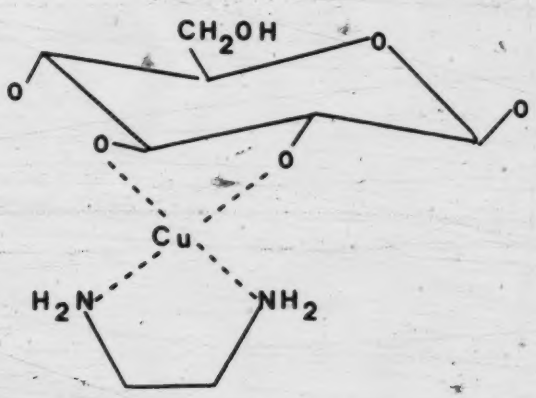


Figure 12. Cuen complex with cellulose glycol group. [Jonhson, 1985, p. 183]

Procedure: The cadoxen was prepared by the procedure proposed by Donetzhuber [1960]. This results in a cadoxen solution containing 28% ethylene diamine, 5.3% cadmium and which is 0.35% with respect to sodium hydroxide.

The intrinsic viscosity was measured following the procedure described by Segal and Timpa [1972]. The dissolution of the cotton samples was carried out at low temperatures (about 5-10C), since it has been observed that dissolution at room temperature tends to result in a cloudy solution, particularly with cotton of higher molecular weight. For each replicate about 0.019 g of cellulose was weighed in a 25 ml erlenmeyer flask. From the same specimen a sample weighing approximately 0.2g was placed in a weighing bottle to determine the moisture content. In order to prevent the formation of gel particles three to four drops of water were added to the cotton [Henley, 1960]. After standing for 5 to 10 minutes to let the water wet the fibres, 10 ml of

cadoxen was added. The mixture was stirred for 1 hour using a magnetic stir bar. Ten ml of distilled water (taking in consideration the water added previously) was added to make 20 ml of a 1:1 cadoxen-water solution. Finally the solution was filtered in a fritted glass filter funnel to remove undissolved impurities.

The viscometric measurements were carried out in a Ubbelohde size 1 viscometer at 25C. The flow time of three different concentrations was determined. The initial concentration of cellulose was 0.09 g/dl, the second 0.06 g/dl and the third one was 0.04 g/dl. First 10 ml of the cellulose solution was added to the viscometer. After waiting 15 minutes to allow the solution to reach temperature equilibrium (25C) a first reading was taken. The two dilutions were done directly in the viscometer by adding 5 ml of the diluent (1:1 cadoxen-water).

The intrinsic viscosity [η] was obtained by finding $[\eta_{rel}]$ for three concentrations and plotting:

$$\log\ [(\eta_{rel} - 1)/c]$$

where: c = concentration (g/dl)

$\eta_{rel} = \frac{t}{t_o}$ (s)

t = outflow time of solution (s)

t_o = outflow time of solvent (s)

versus c (g/dl) and extrapolating the straight line through the points to c = 0. The intercept gives log[η]. From the intrinsic viscosity [η], a viscosity-average degree of polymerization was calculated using the following relationship [Segal and Timpa, 1972][see appendix V]

$$[\eta] = 1.84 \times 10^{-2}(DP)^{0.76} \qquad \text{XXIX}$$

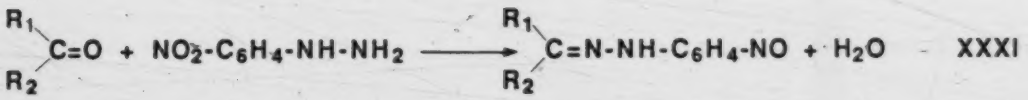
3.5.4. Carbonyl content

The carbonyl content was determined using Blair and Cromie's method [1977] which is a modification of the procedure of Ermolenko and Savastenko [1966]. It is a spectrophotometric method based on the absorption of the p-nitrophenylhydrazones of cellulose. The absorption is calculated on the basis of the reflection spectra according to the Gurevich-Kubelka-Munk relation:

$$f(R) = \frac{k}{s} = \frac{(1-R)^2}{2R} \qquad \text{XXX}$$

where S = scattering
K = absorption coefficient
R = reflectance

During the reaction of the p-nitrophenylhydrazine ($C_6H_7N_3O_2$) [Merck Index, 1983] with the carbonyl groups of the tested cellulose material an orange-yellow product, which is the colored hydrazone or p-nitrophenylhydrazine derivatives, was formed. The reaction below shows the condensation of p-nitrophenylhydrazine with a carbonyl group.



XXXI

Ermolenko and Savastenko [1966, p. 81] note that "aldehydes and alpha-hydroxyketone groups readily react with arylhydrazines at room temperature and under mild conditions. The colored product accordingly contains both arylhydrazones and osazones." For simplicity, the product of that reaction is called p-nitrophenylhydrazone [Ermolenko and Savastenko, 1966]

A linear relationship exists between absorbance of the coloured p-nitrophenylhydrazone and carbonyl content. The maximum absorption of the coloured p-

nitrophenylhydrazone was measured at 400 nm in order to determine the carbonyl content in the sample.

Because the presence of carboxyl groups affects the experimental results [Ermolenko & Savastenko, 1966; Blair and Cromie, 1977; Nevell, 1985], the interference of carboxyl groups was blocked by treatment with a barium chloride solution at pH 7.0 [Blair & Cromie,1977].

Procedure (Blair and Cromie, 1977): Four net bags, each containing a cotton sample of 0.12 g were placed in an excess of reagent consisting of p-nitrophenylhydrazine (0.12 g) in 50% ethanol (160 cc), 2M hydrochloric acid (5.5 cc) diluted to 200 cc with ethanol. The mixture was heated for 3 hours at 60 ±1C. The product was filtered and then washed with ethanol. The four samples were then treated with ethanol in a Soxhlet extractor for 24 hours, followed by a 30 min wash with 0.01M barium acetate and finally washed with water and dried for 2 hours in a vacuum oven at 100C. The absorption spectrum of the sample was determined after dissolving it in 60% cadoxen solution. The dissolved specimen was placed in a 1 cm cell and the absorption at 400nm, was determined. Using the concentration, the absorbance at 400nm and the length of cell (1cm) the specific absorption coefficient (*a*) was calculated.

$$a = \frac{\text{absorbance}}{\text{concentration (g/dl) x length of cell (cm)}} \qquad \text{XXXII}$$

A calibration curve was prepared from data published by Blair and Cromie [1977] and the extinction coefficient was calculated. Using the equation of the calibration curve and the specific absorption coefficient (*a*) the millimoles of carbonyl per 100 g of cellulose was determined. (The calibration curve is shown in Appendix VI).

3.5.5. Carboxyl content

The carboxyl content was determined using the methylene blue method described in the ASTM 1926-63 (reapproved 1985). This method based on a procedure developed by Davidson [1948] has the advantage of being reliable for a whole range of carboxyl values. This makes it particularly useful with oxycellulose of low carboxyl content. Like most of the methods used for determination of the carboxyl content, the use of methylene blue, which is a chloride salt of a strong base [see Figure 13] is based on cation exchange [Nevell, 1985].

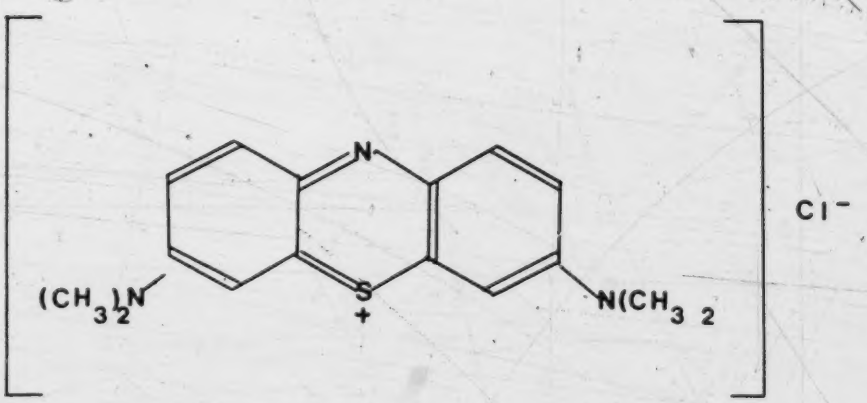


Figure 13. Methylene blue molecule. [Merck Index, 1983]

The methylene blue cation has a stronger affinity for oxycellulose than other cations such as calcium, potassium and barium [Davidson, 1948].

$$Rcell\ COOH + M^+ \rightleftharpoons Rcell\ COOM + H^+ \qquad \text{XXXIII}$$

where M^+ = methylene blue cation.

Methylene blue cations have a great affinity towards acidic cellulose. This allows the establishment of an ion exchange equilibrium with a low concentration of cations of methylene blue [Davidson, 1948]. In order to force the equilibrium to the right the reaction should be conducted at a controlled pH of about 7.8. At that pH the methylene blue absorption and the carboxyl content are equal [Nevell,1985]. The carboxyl content is determined by measuring the concentration of cation in the solution before and after absorption by cotton [Davidson, 1948].

Procedure: The sample was treated with 0.0002M methylene blue solution buffered to a pH of 8 with diethylbarbituric acid (barbital). The buffer solution was prepared by dissolving 1.151 g of diethylbarbituric acid in 1 litre of water, to which was added the equivalent of 0.16 g of sodium hydroxide. The methylene blue stock solution (0.002M) was prepared by dissolving 0.640 g of methylene blue in water, making allowance for moisture, and diluting to 1 litre in a volumetric flask. The methylene blue-buffer solution (0.0002M) was made by mixing 1 volume of the methylene blue stock solution with 1 volume of the buffer stock solution and diluting to a total of 10 volumes in a volumetric flask. A fresh solution was prepared for each determination.

A range of methylene blue-buffer solutions, containing the same amount of buffer but different amounts of methylene blue, was made up to prepare a calibration curve. To ten 100 ml volumetric flasks containing 10 ml of the stock solution of buffer 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 ml of the 0.002M stock solution was added. Each solution was then diluted to the mark with water and mixed thoroughly. Two ml of each of the solutions was pipetted into a 25 ml volumetric flask. Two ml of 1% HCL was added. The solution was then diluted to the mark and mixed. The absorbance of the solution at 620nm was measured with a HP 8451A Diode Array spectrophotometer using quartz cells of 1cm pathlength and distilled water as reference. A new calibration curve was done for each newly prepared 0.002 methylene blue stock solution.

In order to determine the carboxyl content, three samples of cotton (one estimated to give 50% exhaustion, one 10 to 15% smaller and one 10 to 15% larger) were required. The samples to be treated were ravelled and chopped into 3 mm lengths and were weighed in stoppered bottles of about 30 ml capacity. At the same time a sample of the same fabric was weighed and kept in order to determine the moisture content of the cotton and correct sample masses to dry weights. To the bottle containing the test sample, 20 ml of 0.0002M methylene blue buffer solution was added. The bottles were then place on a rotating wheel and agitated over night. After the cotton settled, a 2 ml aliquot of the methylene blue solution was removed with an automatic pipet and was transferred to a 25 ml volumetric flask. Two ml of 1% HCl solution was added. The solution was diluted to the mark, and the absorbance at 620 nm was measured. The sample size that gives 50% exhaustion of methylene blue solution was determined by plotting the sample size (dry mass of cotton) against the concentration of methylene blue solution in the supernatant liquid. From the plot the sample size that gives 50% exhaustion of the dye solution was read. A sample plot is shown in Appendix V.

The calculation of carbonyl content was based on the size of the sample that causes 50% exhaustion of 20 ml of 0.0002M methylene blue solution. This sample has used 0.002 millimoles of methylene blue in ion exchange with carboxyl groups. Therefore the number of millimoles of carboxyl per 100g of cellulose (M) is calculated as follows:

$$M = (0.002/W) \times 100 \qquad \text{XXXIV}$$

where: W = dry mass of specimen (g) to give 50% exhaustion of 20ml of 0.0002M methylene blue solution.

4. RESULTS

In order to evaluate the long term effects of deacidifying agents, calcium hydroxide ($Ca(OH)_2$), magnesium bicarbonate ($Mg(HCO_3)_2$) and methoxy magnesium methyl carbonate (Wei T'o®), on naturally aged cotton, changes in colour, pH, degree of polymerization, carbonyl and carboxyl content have been investigated.

4.1. Statistical analysis

The dependent variables, aqueous extract pH, colour change, carbonyl, carboxyl and degree of polymerization were measured against the independent variables treatments, fabrics and aging in order to see if there was a significant difference among the means of the independent variables.

A three way UANOVA and Duncan's Multiple Range Test (α: 0.05) were carried out using the SPSS-X programme available at the University of Alberta.

4.2. Physical changes: colour change

The reference used to determine colour change (ΔE) was based on the reading of the specimen (L^*, a^*, and b^*) obtained before treatment with deacidifying agents. Immediately after treatment with deacidifying agents, there is only a small change in colour (ΔE = 0.27 to 1.11 CIELAB units) of naturally aged (A,B,C) fabrics.[2] The specimens which were artificially aged by bleaching (D) reacted differently; they yellowed slightly immediately after being treated (ΔE = 5.52 to 7.65). After accelerated aging for 15 days at 100C, 100% RH, the colour change of the heated fabrics was uniform throughout the fabric except for a few specimens showing water stains at the bottom. Some specimens of the fabrics A, B, and C had dark spots. These spots were

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[2] A colour change of about 1 CIELAB unit is visible to the eyes [Jennings, 1984]

probably caused by the presence of an impurity such as a rust particle on the fabric which could have acted as an oxidizing catalyst during the aging.

Upon aging in the presence of heat and moisture, all the cotton fabrics darkened, but the intensity was different according to the type of fabric. Fabric A, B, and C turned beige while fabric D turned various shades of brown according to the treatment received. Table 3 shows the results in colour change at 0 and 15 days for all fabrics.

Table 3. Colour change[1] of alkaline-buffered naturally and artificially aged cotton.

fabric	treatment	ΔE (CIELAB units) 0 days	s[5]	15 days	s
A[3]	water(control)	0.00		18.65	2.00
	MMMC[2]	0.91	0.07	17.06	3.62
	$Mg(HCO_3)_2$	0.44	0.15	14.35	2.30
	$Ca(OH)_2$	0.54	0.21	12.93	2.14
B[3]	water(control)	0.00		15.38	0.44
	MMMC[2]	0.67	0.16	17.23	0.66
	$Mg(HCO_3)_2$	0.27	0.11	14.13	0.84
	$Ca(OH)_2$	0.54	0.14	16.12	0.47
C[3]	water(control)	0.00		21.08	2.51
	MMMC[2]	1.10	0.14	18.64	1.03
	$Mg(HCO_3)_2$	0.33	0.04	17.61	0.84
	$Ca(OH)_2$	0.46	0.07	18.38	1.98
D[4]	water(control)	0.00		42.80	1.73
	MMMC[2]	5.53	0.15	35.44	1.49
	$Mg(HCO_3)_2$	7.36	0.16	33.93	0.73
	$Ca(OH)_2$	7.65	0.36	34.00	0.95

[1] Average of ten replicates.
[2] Methoxy magnesium methyl carbonate (Wei T'o® solution #2).
[3] Naturally aged fabric.
[4] Artificially aged fabric.
[5] Standard deviation

After aging, there is a significant difference in colour change in relation to treatment (Table 4). In general the control (water treated) specimens exhibited a greater colour change than the alkaline buffered specimens. This difference among the

control and alkaline buffered fabrics is most noticeable for the artificially aged fabric(D); the alkaline buffered fabrics registered a colour change ranging from ΔE = 33.99 to 35.44 CIELAB units, while the control specimens had a colour difference of 42.80 CIELAB units. The greatest colour difference obtained by D (artificially aged) can be explained by a greater tendency to yellowing due to the severe bleaching treatment that it received. Nevell [1986] reports that cotton bleached with hypochlorite under acidic or neutral conditions turns yellow with time even at room temperature and that the presence of aldehyde groups favours yellowing of cellulose during heating at 100C. He adds that the yellowing of oxycellulose with aldehyde groups is enhanced in the presence of alkali. It is interesting to note that in this experiment the alkaline buffered fabrics present a lesser change upon heating than water treated (control) fabrics. The results do not

Table 4. Mean colour difference[1](CIELAB units) of alkaline-buffered cotton after aging. Homogeneous subsets as determined by Duncan's Multiple Range Test (α = 0.05) are underlined.

fabric	treatment[2]				null hypothesis
	Ca	Mg	M	W	reject
A[3]	12.93	14.35	17.06	18.65	
	Mg	W	Ca	M	reject
B[3]	14.13	15.38	16.12	17.23	
	Mg	Ca	M	W	reject
C[3]	17.61	18.38	18.64	21.08	
	Mg	Ca	M	W	reject
D[4]	33.93	34.00	35.44	42.80	

[1] Average of 10 samples.
[2] Ca = $Ca(OH)_2$; Mg = Mg $(HCO_3)_2$;; M = Methoxy magnesium methyl carbonate (Wei T'o® solution #2); W = Water (control).
[3] Naturally aged fabric.
[4] Artificially aged fabric.

agree with Peacock [1980] who found that fabric treated with deacidifying agents such as $Mg(HCO_3)_2$ and MMMC had a greater colour change after aging than the untreated fabric. Of the deacidifying agents used, the MMMC showed the greatest variation in colour upon aging. This confirms the finding of Kerr [1982]. Table 5 shows a summary of the findings of Peacock [1980] and Kerr [1982].

Table 5. Colour difference ΔE (NBS units) of alkaline-buffered cellulosic fabrics before and after aging.

source	treatment	aging		material
		before	after	
Peacock [1980]	water(control)	0.0	1.5[2]	artificially aged linen
	MMMC[1]	2.1	5.1	
	$Mg(HCO_3)_2$	3.9	5.1	
Kerr [1982]	water(control)	0.00	20.39[3]	new cotton
	MMMC[1]	0.84	13.08	
	$Mg(HCO_3)_2$	0.44	10.58	
	$Ca(OH)_2$	0.40	12.88	

[1] Methoxy magnesium methyl carbonate (Wei T'o® solution #2).
[2] Samples conditioned to 50% R.H. for 24 hours, heat sealed and heated at 70C for 21 days.
[3] Sample sealed in a pressure test tube and heated at 100C in 100% R.H. for 15 days.

Other authors reported yellowing of cellulose upon aging [Farquhar, 1956; Peters and Still, 1978; Achwall and Murali, 1986] Even if the cause of yellowing has not been clearly established, it is usually related to the formation of functional groups such as carbonyl groups and conjugated double bonds. Albeck et al [1965] explained the yellowing tendency of oxidized and hydrolyzed cotton solely by the presence of aldehyde groups and particularly by the one on C_1. They did not observe any influence from ketone and carboxyl groups. Achwall and Murali [1986] studied the yellowing of bleached bamboo pulp and oxidized pulp submitted to accelerated aging by heating and steaming. They found an increase in yellowing due to the presence of both free carboxyl and

reducing groups in oxycellulose. In the section on chemical changes more details in relation to each functional group (carbonyl and carboxyl) are presented.

4.3. Chemical changes

4.3.1. Aqueous extract pH

Table 6 shows the pH values for the cold aqueous extract of alkaline-buffered cotton.

Table 6. Aqueous extract pH[1] of alkaline-buffered naturally and artificially aged cotton.

fabric	treatment	pH			
		0 day	s[5]	15 days	s
A[3]	water(control)	6.1	0.1	5.1	0.1
	MMMC[2]	10.2	0.0	9.1	0.1
	$Mg(HCO_3)_2$	10.4	0.1	8.8	0.1
	$Ca(OH)_2$	9.5	0.0	8.4	0.0
B[3]	water(control)	6.1	0.0	5.3	0.1
	MMMC	10.3	0.0	9.0	0.2
	$Mg(HCO_3)_2$	10.2	0.2	8.3	0.1
	$Ca(OH)_2$	9.5	0.1	8.5	0.1
C[3]	water(control)	6.3	0.1	4.7	0.0
	MMMC	10.3	0.1	9.3	0.2
	$Mg(HCO_3)_2$	10.4	0.1	7.4	0.0
	$Ca(OH)_2$	9.4	0.1	7.8	0.1
D[4]	water(control)	5.9	0.1	3.8	0.0
	MMMC	10.3	0.0	7.5	0.1
	$Mg(HCO_3)_2$	10.2	0.0	6.6	0.0
	$Ca(OH)_2$	9.4	0.1	7.8	0.1

[1] Average of two samples.
[2] Methoxy magnesium methyl carbonate (Wei T'o® solution #2).
[3] Naturally aged fabric.
[4] Artificially aged fabric.
[5] Standard deviation

The initial aqueous extract pH value of all the fabrics is slightly acidic, the values ranging from 5.9 to 6.3; the artificially aged fabric (D), however, has the lowest

initial pH of 5.9. After treatment with deacidifying agents, the pH increased for all fabrics, the MMMC and $Mg(HCO_3)_2$ treatments giving the fabrics the highest pH values (pH 10.2-10.4)

After aging, the water treated fabrics in all cases are characterized by an increase in acidity. The water-treated control specimen of fabric D had the lowest pH (3.8) and showed the greatest change (Δ 2.1) compared to the initial measurement. The pH values of the alkaline buffered fabrics decreased upon aging; however, except for fabric D treated with $Mg(HCO_3)_2$ (pH: 6.6), the values do not fall below 7.4. The least variation after treatment for both 0 and 15 days aging was obtained by the $Ca(OH)_2$ treatment.

Table 7. Mean (n=2) of cold aqueous extract pH of alkaline-buffered cotton after aging. Homogeneous subsets as determined by Duncan's Multiple Range Test (α = 0.05) are underlined.

fabric	treatment[1]				null hypothesis
	W	Ca	Mg	M	
A	5.1	8.4	8.8	9.1	reject
	W	Mg	Ca	M	
B	5.3	8.3	8.5	9.0	reject
	W	Mg	Ca	M	
C	4.7	7.4	7.8	9.3	reject
	W	Mg	M	Ca	
D	3.8	6.6	7.5	7.8	reject

[1] W = Water; Ca = $Ca(OH)_2$; Mg = $Mg(HCO_3)_2$; M = methoxy magnesium methyl carbonate (Wei T'o® solution #2).

The results obtained for the MMMC and $Mg(HCO_3)_2$ treatment, are consistent with those obtained by Kerr [1982] and Jennings [1984]. With these two deacidifying agents Peacock [1980] has a lower pH recorded both before and after aging. The difference may be caused by the use of different pH measurement method or by residual acid in her specimens following artificial aging (acid hydrolysis). The values for the specimens

treated with $Ca(OH)_2$ are slightly higher than those obtained by Kerr, but in both cases the $Ca(OH)_2$ treated fabric showed the least variation after treatment and after aging. The pH values obtained by Peacock [1980], Kerr [1982], and Jennings [1984] are reported in Table 8.

Table 8. Aqueous extract or surface pH of alkaline-buffered cellulosic fabrics.

source	treatment	before aging	after aging	fabric
Jennings[1] [1984]	water	7.5	N/A	naturally aged cotton
	MMMC	10.5	N/A	
	$Mg(HCO_3)_2$	10.5	N/A	
Kerr[2] [1982]	water	7.04	4.84[4]	new cotton
	MMMC	10.30	9.30	
	$Mg(HCO_3)_2$	10.11	8.82	
	$Ca(OH)_2$	7.80	7.79	
Peacock[3] [1980]	water	4.0	3.4[5]	artificially aged linen
	MMMC	9.2	6.0	
	$Mg(HCO_3)_2$	8.8	6.8	

[1] Aqueous extract pH (Tappi method).
[2] Hot aqueous extract pH.
[3] Surface pH measurement according to Kelly [1972].
[4] Samples sealed in a pressure test tube and heated at 100C in 100% R.H. for 15 days.
[5] Samples conditioned to 50% R.H. for 24 hours, heat sealed and heated at 70C for 21 days.

4.3.2. Degree of polymerization

A reduction of the degree of polymerization which results from the scission of the glycosidic bond can be produced by acid (hydrolysis) or by alkali (alkaline scission) [Nevell, 1985]. The former results from exposure to concentrated or hot diluted acid [Fan et al, 1987]. In the latter case, random scission of the glycosidic bond has been observed when cellulose is treated with hot alkali. According to Golova and Nosova [1973] alkaline scission occurs usually at temperatures above 150C. This reaction is neither due to oxidation nor to thermal degradation but to the action of hydroxyl ion

[Corbett, 1958]. Oxidized celluloses are more likely to undergo this reaction than cotton containing no carbonyl groups [Corbett, 1960].

The degree of polymerization of specimens, reported in Table 9, was determined from intrinsic viscosity measurements (Appendix VI). Analysis of variance indicated

Table 9. Degree of polymerization[1] of alkaline-buffered naturally and artificially aged cotton.

fabric	treatment	DP			
		0 day	s	15 days	s
A[3]	water(control)	3341	54	1089	1
	MMMC[2]	3859	453	1840	296
	$Mg(HCO_3)_2$	2956	294	1829	523
	$Ca(OH)_2$	3349	268	1955	171
B[3]	water(control)	1620	107	1182	120
	MMMC[2]	1537	160	1235	94
	$Mg(HCO_3)_2$	1584	233	1177	72
	$Ca(OH)_2$	1674	137	1436	13
C[3]	water(control)	2440	465	679	25
	MMMC[2]	2741	218	1320	1
	$Mg(HCO_3)_2$	2440	71	1583	181
	$Ca(OH)_2$	2815	173	1349	139
D[4]	water(control)	306	12	154	7
	MMMC[2]	291	27	237	21
	$Mg(HCO_3)_2$	266	10	221	9
	$Ca(OH)_2$	287	11	240	1

[1] Mean of two replicates.
[2] Methoxy magnesium methyl carbonate, commercially available as Wei T'o® solution #2 .
[3] Naturally aged fabric.
[4] Artificially aged fabric.

that there is a significant difference among treatments before and after the aging period (see Table 10). Concerning the treatments, there is a significant difference (0.05 level) between the water treated (control) and alkaline buffered fabrics in most cases,

however, there is not significant difference among the three alkaline buffered ($Ca(OH)_2$, $Mg(HCO_3)_2$ and MMMC) treatments.

Table 10. Mean degree of polymerization of alkaline-buffered cotton after accelerated aging Homogeneous subsets as determined by Duncan's Multiple Range Test (α = 0.05) are underlined.

fabric	treatment[1]				null hypothesis
A[2]	W 1089	Mg 1829	M 1840	Ca 1955	reject
B[2]	Mg 1177	W 1182	M 1235	Ca 1436	accept
C[2]	W 679	M 1320	Ca 1349	Mg 1583	reject
D[3]	W 154	Mg 221	M 237	Ca 240	reject

[1] Mg = $Mg(HCO_3)_2$; M = Methoxy magnesium methyl carbonate (Wei T'o ®solution #2); Ca = $Ca(OH)_2$; W = Water.
[2] Naturally aged fabric.
[3] Artificially aged fabric.

Except for fabric B treated with calcium hydroxide all fabrics showed a significant decrease in the degree of polymerization after accelerated aging at 100C and 100%RH. Regardless of the type of treatment, alkaline buffered fabrics A, C and D show less degradation upon aging than the water (control) treated fabrics. There is no significant difference among treatments for fabric B. For all properties measured, this fabric presented the least change upon aging. All fabrics, except C, buffered with calcium hydroxide had a somewhat higher degree of polymerization after aging than fabrics treated with the other agents.

A reduction in the degree of polymerization is often reported after accelerated aging at low temperatures (below 150C). Previous research on alkaline-buffers used in conservation [Kerr, 1982; Burgess, 1986] led to a different conclusion concerning the ability of deacidifying agents to prevent chain scission in naturally aged and artificially aged cellulosics.

While the results of this study are consistent with those obtained by Kerr [1982] they do not agree with the results of Burgess [1986]. Burgess obtained poor results for cotton buffered with calcium hydroxide while cotton treated with calcium sulfate and Ottawa tap water showed less decrease in DP during aging. Burgess explains the important change in degree of polymerization with calcium hydroxide by the great increase in sensitivity of naturally aged cellulose to alkaline materials. Kerr conducted her test on new cotton which was treated before accelerated aging, while Burgess was working with naturally aged fabric consisting of Peruvian cotton dating from about A.D 1100 to A.D. 1350.

4.3.3. Carbonyl

A summary of carbonyl content for each fabric and treatment is reported in Table 11. Of all the fabrics only D (artificially aged) shows a significant difference in carbonyl content (0.05 level) upon aging. After aging, all other fabrics showed little change in carbonyl content whether they were treated with deacidifying agents or water. Perhaps a longer aging period would have brought greater changes in carbonyl content.

For fabric D, both the water treated (control) and alkaline-buffered cotton showed a decrease of carbonyl content upon aging. This result was unexpected. The decrease, however, is greater for the alkaline-buffered samples than the water treated control. Of the three buffers tested, methoxy magnesium methyl carbonate (Wei T'o®) produced the lowest carbonyl content (0.342 mM/100 g) after aging.

Formation of carbonyl groups were previously observed upon heating of cellulosic material [Burgess, 1980; Kerr, 1982]. The low carbonyl content of heated specimens recorded here could be attributed to :

1. Further oxidation of carbonyl groups to carboxyl groups. If this has happened, an increase should be observed in carboxyl content, unless decarboxylation occurs upon aging.

Table 11. Carbonyl content[1] (mM/100 g) of alkaline-buffered naturally and artificially aged cotton.

fabric	treatment	carbonyl [mM/100 g] 0 day	s[5]	15 days	s
A[3]	water(control)	0.173	0.043	0.176	0.018
	MMMC[2]	0.070	0.017	0.109	0.024
	$Mg(HCO_3)_2$	0.094	0.022	0.087	0.103
	$Ca(OH)_2$	0.065	0.013	0.142	0.019
B[3]	water(control)	0.117	0.0097	0.060	0.011
	MMMC[2]	0.087	0.009	0.102	0.023
	$Mg(HCO_3)_2$	0.072	0.025	0.071	0.011
	$Ca(OH)_2$	0.073	0.015	0.112	0.011
C[3]	water(control)	0.226	0.030	0.235	0.025
	MMMC[2]	0.137	0.015	0.108	0.008
	$Mg(HCO_3)_2$	0.165	0.025	0.101	0.016
	$Ca(OH)_2$	0.184	0.016	0.160	0.028
D[4]	water(control)	2.660	0.087	1.714	0.077
	MMMC[2]	2.117	0.033	0.342	0.061
	$Mg(HCO_3)_2$	2.246	0.089	0.491	0.083
	$Ca(OH)_2$	1.591	0.168	0.555	0.037

[1] Mean of three or four replicates.
[2] Methoxy magnesium methyl carbonate, commercially available as Wei T'o® solution #2.
[3] Naturally aged fabric.
[4] Artificially aged fabric.
[5] Standard deviation.

2. The formation of carbon monoxide and dioxide due to decarboxylation and decarbonylation. This reaction is usually reported at higher temperatures (170C) [Shafizadeh, 1985], however, this does not exclude the possibility that it happened at the lower aging temperature (100C).

3. Degradation of the chain due to the detachment of a reducing unit (carbonyl) from the end of a cellulose chain and/or the scission of the chain upon aging. This reaction is enhanced in the presence of alkali, and could have produced water soluble molecules which could have been washed away. A dark-brown residue with a sweet odour, and yellow colour of the water at the bottom of the aging test tubes were noted at the end of the 15 day accelerated aging period for fabric D. These are indicators of decomposition of the cellulose into water soluble molecules.

Table 12. Mean (n=3 or 4) carbonyl content of alkaline-buffered cotton after accelerated aging Homogeneous subsets as determined by Duncan's Multiple Range Test (α = 0.05) are underlined.

fabric	treatment[1]				null hypothesis
	Mg	M	Ca	W	
A[2]	0.087	0.109	0.142	0.176	accept
	W	Mg	M	Ca	
B[2]	0.060	0.071	0.102	0.112	accept
	Mg	M	Ca	W	
C[2]	0.101	0.108	0.160	0.235	reject
	M	Mg	Ca	W	
D[3]	0.342	0.491	0.555	1.714	reject

[1] Mg = $Mg(HCO_3)_2$; M = Methoxy magnesium methyl carbonate (Wei T'o® solution #2); Ca = $Ca(OH)_2$;. W = Water.

[2] Naturally aged fabric.

[3] Artificially aged fabric.

4.3.4. Carboxyl

The summary of carboxyl content before and after aging is presented in Table 13. Immediately after treatment, the naturally aged fabrics showed a slight decrease in their carboxyl content. The decrease is not observed in fabric D (artificially aged) which was initially the most oxidized of all the fabrics.

Table 13. Carboxyl content[1] of alkaline-buffered naturally and artificially aged cotton.

fabric	treatment	carboxyl [mM/100 g]			
		0 day	s[5]	15 days	s
A[3]	water(control)	1.518	0.200	1.325	0.115
	MMMC[2]	1.187	0.100	1.275	0.086
	$Mg(HCO_3)_2$	1.296	0.123	1.112	0.071
	$Ca(OH)_2$	1.154	0.132	0.996	0.069
B[3]	water(control)	1.194	0.053	1.190	0.079
	MMMC[2]	0.925	0.044	1.055	0.004
	$Mg(HCO_3)_2$	1.102	0.118	1.200	0.118
	$Ca(OH)_2$	0.871	0.023	0.888	0.003
C[3]	water(control)	2.098	0.248	1.513	0.055
	MMMC[2]	1.611	0.261	1.503	0.222
	$Mg(HCO_3)_2$	1.636	0.084	1.656	0.164
	$Ca(OH)_2$	1.755	0.304	1.253	0.112
D[4]	water(control)	3.534	0.105	3.145	0.234
	MMMC[2]	3.371	0.051	2.855	0.199
	$Mg(HCO_3)_2$	3.553	0.188	3.740	0.098
	$Ca(OH)_2$	3.645	0.031	3.056	0.179

[1] Mean of three or four replicates.
[2] Methoxy magnesium methyl carbonate (Wei T'o® solution #2).
[3] Naturally aged fabric.
[4] Artificially aged fabric.
[5] Standard deviation.

After aging for 15 days, even if there is a slight decrease in the amount of carboxyl groups in the naturally aged fabrics (A, B, and C), only D (artificially aged) exhibits a significant change. Rather than increasing in carboxyl content as expected, the carboxyl

content of D decreased with heating. The same drop in carboxyl content was reported by Kerr [1982]. There are several possible reasons why the carboxyl content might decrease during 15 days of heating at 100C, 100% RH:

1. Decarboxylation due to the formation of carbon monoxide and carbon dioxide during heating [Shafizadeh, 1985].
2. Scission of cellulose chains ,leading to the formation of small water soluble compounds. These could have been removed from the cotton during the reaction with Mb^+ solution.

Table 14. Mean carboxyl content (mM/100 g) of alkaline-buffered cotton after aging. Homogeneous subsets as determined by Duncan's Multiple Range Test (α = 0.05) are underlined.

fabric	treatment[1]				null hypothesis
A[2]	Ca 0.996	Mg 1.112	M 1.275	W 1.325	reject
B[2]	Ca 0.888	M 1.055	W 1.190	MG 1.200	reject
C[2]	Ca 1.253	M 1.503	W 1.513	Mg 1.656	reject
D[3]	M 2.855	Ca 3.056	W 3.145	MG 3.743	reject

[1] Ca = $Ca(OH)_2$; Mg = $Mg(HCO_3)_2$; M = Methoxy magnesium methyl carbonate (Wei T'o® solution #2); W = Water.
[2] Naturally aged fabric.
[3] Artificially aged fabric.

5. DISCUSSION

Textile conservators do not always have the opportunity to undergo tests in order to determine the level of degradation of a textile. Moreover, most of the tests used to determine chemical degradation employ techniques requiring the destruction of specimens. The measurement of pH appears to be useful to determine the condition of a textile. In this study a positive correlation was found between pH and degree of polymerization for a given fabric. The unbuffered (water-treated) specimens of fabric A, C, and D, for example, exhibited both the lowest pH values and the greatest decrease in degree of polymerization after accelerated aging, which indicates that the accumulation of acidic degradation products during aging causes chain scission (see table 15). This finding is in agreement with a study conducted by Arney and Chapdeleine [1981] in which it was found that deacidification with alkaline agents is an effective means for inhibiting the aging process. However, no difference was found in the efficiency of one deacidifying agent over another. The pH measurement of specimens provides a good indication of degradation, since fabrics of low pH values are more likely to suffer from auto-hydrolysis and environmental acidity.

The yellowing of the cellulose which occurs upon heating is related to the formation of functional groups, such as carbonyl. Thus the level of yellowing would be expected to be directly proportional to the concentration of functional groups present in the fabric after accelerated aging. Although a significant change in colour was observed after heating, in general, there was no correlation between yellowing and carbonyl groups. Only the naturally aged fabric C and artificially aged fabric D showed a direct relationship between yellowing and the number of carbonyl groups present. For both fabrics, the water treated specimens showed the greatest yellowing and the greatest concentration of carbonyl groups after aging.

In spite of the fact that in paper conservation the practice of deacidification has become more and more accepted, textile conservators are still reluctant to apply deacidifying treatments to naturally aged textiles. This apprehension originates from the fact that the research done on the subject mainly involves the use of new or artificially aged fabrics. There is a lack of certainty in applying findings obtained from work done with artificially aged fabrics to naturally aged fabrics. It is suspected that artificial aging does not reproduce adequately what would happen over many years of use. Artificial aging provides much more uniform results after deacidification which could lead to a simplification in the interpretation of what happened. With an artificially aged fabric, according to the aging process, it is possible to speculate on the level and type of oxidation present in the fabric. A naturally aged fabric has an unknown history, making difficult the interpretation of its condition.

In this study a comparison of the data obtained with naturally aged (A, B, and C) and artificially aged (D) fabrics showed that there are differences in the response of the fabrics to deacidification and further aging [see Table 15]. For fabric D (artificially aged by bleaching) every property which was measured showed a significant difference upon aging, but this was not necessarily the case with fabrics A, B, anc C, the naturally aged fabrics. Fabrics A and B which were the least degraded and showed the least change upon aging. For fabric A, the water-treated control was always more degraded than the alkaline buffered specimens thus, the finishes offered some protection to this fabric. For fabric B, the water-treated control and the alkaline buffered specimens responded the same way to accelerated aging (except for pH). Fabric C, which was the most degraded of the naturally aged fabrics, is the one which had the greatest similarity to fabric D, the most severely degraded fabric. The initial level of degradation, therefore, is an important factor in deciding whether to deacidify a fabric. The findings of this study suggest that fabrics which are highly degraded have the most positive response to the deacidifying treatment, that is, the fabric properties are most likely to benefit from

the treatment. It is also apparent from this research that knowledge of the initial degradation helps a researcher select appropriate accelerated aging conditions. If a fabric is not particularly damaged, a longer aging period (than 15 days at 100C, 100% RH) is required to obtain sig nificant differences in properties after accelerated aging.

Table 15: Δ carbonyl, Δ carboxyl, and %decrease in degree of polymerization of naturally and artificially aged fabrics after 15 days of aging.

	carbonyl mM/100g			carboxyl mM/100g			DP		
	$C{=}O_0$	$C{=}O_{15}$	$\Delta C{=}O$	$COOH_0$	$COOH_{15}$	$\Delta COOH$	DP_0	DP_{15}	%decrease
control									
A	0.17	0.18	+0.01	1.5	1.3	-0.2	3341	1089	67
B	0.17	0.06	-0.11	1.2	1.2	0.0	1620	1182	27
C	0.22	0.24	+0.02	2.1	1.5	-0.6	2440	679	70
D	2.70	1.70	-1.00	3.5	3.1	-0.4	306	154	50
Wei T'o									
A	0.07	0.11	+0.04	1.2	1.3	+0.1	3859	1840	52
B	0.09	0.10	+0.01	0.9	1.1	+0.2	1537	1235	20
C	0.14	0.11	-0.03	1.6	1.5	-0.1	2741	1320	52
D	2.10	0.30	-1.80	3.4	2.9	-0.5	291	237	19
$MG(HCO_3)_2$									
A	0.09	0.08	-0.01	1.3	1.1	+0.2	2956	1829	38
B	0.07	0.07	0.00	1.1	1.2	+0.1	1584	1177	26
C	0.16	0.10	-0.06	1.6	1.7	+0.1	2440	1583	35
D	2.20	0.50	-1.70	3.6	3.7	+0.1	266	221	17
$Ca(HO)_2$									
A	0.06	0.01	-0.05	1.2	0.9	-0.3	3349	1955	42
B	0.07	0.11	+0.04	0.9	0.9	0.0	1674	1436	14
C	0.16	0.10	-0.06	1.8	1.3	-0.5	2815	1349	52
D	1.60	0.60	-1.00	3.6	3.1	-0.5	287	240	16

6. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH

6.1 Summary

This research project was designed to determine whether naturally aged cotton textiles are chemically damaged by treatment with selected deacidifying agents. Specific variables were tested in order to verify the validity of the null hypotheses.

In order to determine whether there are physical and chemical changes due to the use of deacidifying agents on naturally aged cotton fabrics, the colour, pH, degree of polymerization, carbonyl and carboxyl content were investigated immediately after treating the fabrics and after accelerated aging. Three naturally aged fabrics (bed sheets) and one fabric artificially aged by chlorine bleaching were treated with the following deacidifying agents: methoxy magnesium methyl carbonate (Wei T'o® #2), magnesium bicarbonate ($Mg(HCO_3)_2$), and calcium hydroxide ($Ca(OH)_2$); specimens of each fabric were treated with distilled water as control. The long term effects were estimated by exposing specimens of each treated fabric to an accelerated aging at 100C, 100% RH for 15 days.

Null Hypothesis1: There is no significant difference in the colour of naturally aged cotton after deacidification.

All fabrics yellowed after 15 days of accelerated aging; there was a significant difference in colour after aging depending on the treatment the fabrics received. The water treated control for fabrics A, C, and D exhibited the greatest change upon aging. For fabric B, a sheet of unknown history, specimens treated with calcium hydroxide ($Ca(OH)_2$) and methoxy magnesium methyl carbonate (Wei T'o®) exhibited a greater colour change after aging and higher carbonyl content than the water treated (control). The higher carbonyl content confirm the fact that the yellowing of fabric B was

indicative of the presence of new functional groups, such as carbonyl, which developed upon oxidation of the cellulose [Albeck,1975; Achwal and Murali, 1986].

Null hypothesis 2: There is no significant difference in the pH of aqueous extracts of naturally aged cotton after deacidification.

All fabrics became more acidic during accelerated aging. There was a significant difference in the aqueous extract pH between the various deacidifying treatments before and after aging for all fabrics. The pH, both initial and after 15 days of aging, was lowest when fabrics A, B, C, and D were treated with water only. Not only did the deacidifying agents neutralize acidity present in fabrics immediately after treatment but they also diminished the risk of acidification of the fabric upon aging. By leaving an alkaline reserve in the fabric, the deacidifying agents inhibited the aging process [Arney and Chapdeleine, 1981]

Null hypothesis 3: There is no significant difference in the intrinsic viscosity and the degree of polymerization of naturally aged cotton after deacidification.

The deacidifying agents assured protection during aging because they prevented chain scission. A significant difference in the intrinsic viscosity and the degree of polymerization (DP) was found after aging among fabrics treated with the various deacidifying treatments and water. The water treated (control) specimens had a lower DP than the alkaline buffered specimens indicating more chain scission had occured. For the naturally aged fabric B the DP of the water-treated control was not significantly different from the alkaline buffered specimens.

Null hypothesis 4: There is no significant difference in the carbonyl content of naturally aged cotton after deacidification.

There was a slight decrease in the carbonyl content of all the fabrics immediately after treatment with the deacidifying agents. This may be caused in part by an experimental error introduced during the determination of the concentration because allowance was not made for an increase in weight of the fabric following treatment with deacidifying agents. According to Jennings [1984] a weight increase of approximately

2% to 5% may occur after a fabric is treated. There was a significant difference in the carbonyl content between water and deacidifying treatments after aging for naturally aged fabric C and artificially aged fabric D. For these fabrics the water treated control specimens showed a lower carbonyl content than the alkaline buffered specimens, but there was no difference in the carbonyl content of fabrics treated with the various deacidifying treatments. The naturally aged fabrics A and B do not exhibit a significant difference in carbonyl content among water treated and deacidified specimens. The initial level of oxidation of fabrics C and D was greater than for fabrics A and B. This could have made them more likely to undergo changes upon aging and may explain why they were the only ones to show differences between deacidifying treatments after aging. The decrease in carbonyl content of specimens from fabric D (the overbleached cotton) is not clearly understood, because it was expected that the carbonyl content would increase during aging.

Null hypothesis 5: There is no significant difference in the carboxyl content of naturally aged cotton after deacidification.

In general, the carboxyl content of both alkaline-buffered specimens and water-treated controls was lower after aging for 15 days than immediately after treatment. As a result of the various treatments, there was a significant difference in the carboxyl content of all fabrics after aging. For naturally aged fabrics B, C and artificially aged fabric D, the specimens treated with magnesium bicarbonate ($Mg(HCO_3)_2$) had the highest carboxyl values. The highest carboxyl values for the naturally aged fabric A were obtained by the water treated (control) specimens.

It is difficult to interpret the data for the carbonyl and carboxyl contents because the expected increase in carbonyl and carboxyl groups during heating of cellulose [Shafizadeh, 1985] was not observed. There are several reasons why these functional groups might decrease in concentration:

1. Further oxidation of the carbonyl groups to carboxyl groups would lead to a decrease in carbonyl content. However, there is no evidence that this reaction occurred here.

2. The formation of carbon monoxide (CO) and carbon dioxide(CO_2) could result in decarbonylation and decarboxylation of the cellulose.

3. Degradation of the cellulose molecule by a peeling reaction and/or scission of the glycosidic bond would have favoured the formation of small water soluble molecules. Unfortunately no tests were done to identify the gases formed in the aging chamber nor was the water in the aging chamber analyzed for sugar and soluble acids.

6.2. Conclusions

There are two key questions which conservators ask about deacidifying agents: (1) do they damage naturally aged fabrics and (2) will they protect a naturally fabric from further degradation over a long period of time.

The results of this study indicate that if a fabric is not severely damaged, there is no adverse effect after treatment and aging. Since a naturally aged fabric with a high level of degradation was not available, an artificially aged fabric (cotton overbleached with sodium hypochlorite at pH 7) was substituted. It yellowed noticeably during the deacidification treatments, but during accelerated aging, the water-treated control darkened much more than the deacidified specimens. In addition, the water-treated control became more acidic and the DP decreased more than the buffered specimens.

The deacidification treatments appear to protect naturally aged fabrics. The alkaline reserve left by the treatments appears to prevent auto-hydrolysis, neutralize environmental acids and slow down the rate of degradation by hydrolysis and oxidation.

6.3. Recommendations for further research

As a result of this research, some questions more or less directly related to the project itself were raised. Concerning the test methods used in the experimental work, it appears that there is a need to develop an improved technique for measuring the pH of textiles, since it is very useful in assessing degradation. A simpler method for measuring carbonyl content would be useful in order to diminish the risk of experimental error and facilitate comparisons between different studies. It would also be interesting to analyze the gases which evolved from fabrics during accelerated aging in order to interpret changes in the functional groups, and the water in the aging chamber, to determine the sugars and soluble degradation products.

The differences in the response to deacidification observed between naturally and artificially aged fabrics suggest the need to pursue research on highly degraded naturally aged cellulosic textiles.

As reversibility is often considered an essential condition when selecting treatments for conservation purposes, research should be done to determine the reversibility of various deacidifying treatments.

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Appendix I

Description of naturally aged cellulosic textiles

Description of naturally aged cellulosic textiles

Fabric	Description	Condition	pH[1]	Source
A	bed sheet	good condition	6.0	Dr Nancy Kerr
B	bed sheet	yellowed areas and weakened area	6.1	U of A (HCC)[2]
C	bed sheet	good condition	6.3	Dr Betty Crown

[1] Cold aqueous extract pH before application of deacidifying agents.
[2] University of Alberta Historic Costume and Textile Study Collection

Appendix II

Bleaching

Bleaching

The bleaching process was done with a sodium hypochlorite solution (~ 1.5% available chlorine) at room temperature. The sodium hypochlorite bleach bath was prepared following the method described by Burgess [1979]. The bleaching solution (pH 7.0) was made by the addition of 750 ml diluted acetic acid (1:4 glacial acetic acid: water) to a suitable amount (≈ 7 litres) of a stock solution of NaOCl (laboratory grade, 5.25% available chlorine) and diluted with 13 litres of distilled water to a volume of 20 litres.

Prior to bleaching, the two pieces of cotton (95 cm weft x 100 cm warp) were immersed for 10 minutes in distilled water in order to swell the fibres. Once removed from the soaking bath, the excess of water was removed by blotting the cotton between towels. The pieces of cotton were then placed in the bleach bath for 30 minutes. The liquor ratio (bleach liquor volume to cotton weight) was about 100:1. During the bleaching the fabric was gently pressed from time to time. After 30 minutes the cotton was removed and the bleaching reaction was terminated by rapid immersion in two antichlor baths (2,350ml each) of fresh 2% sodium thiosulfate solution. While the fabric was soaking in the sodium thiosulfate bath it was pressed from time to time. After 25 minute it was removed and rinsed in running distilled water for 30 minutes in order to remove the residual chemicals. Another rinse of 30 minutes in distilled was done the following day.

Appendix III

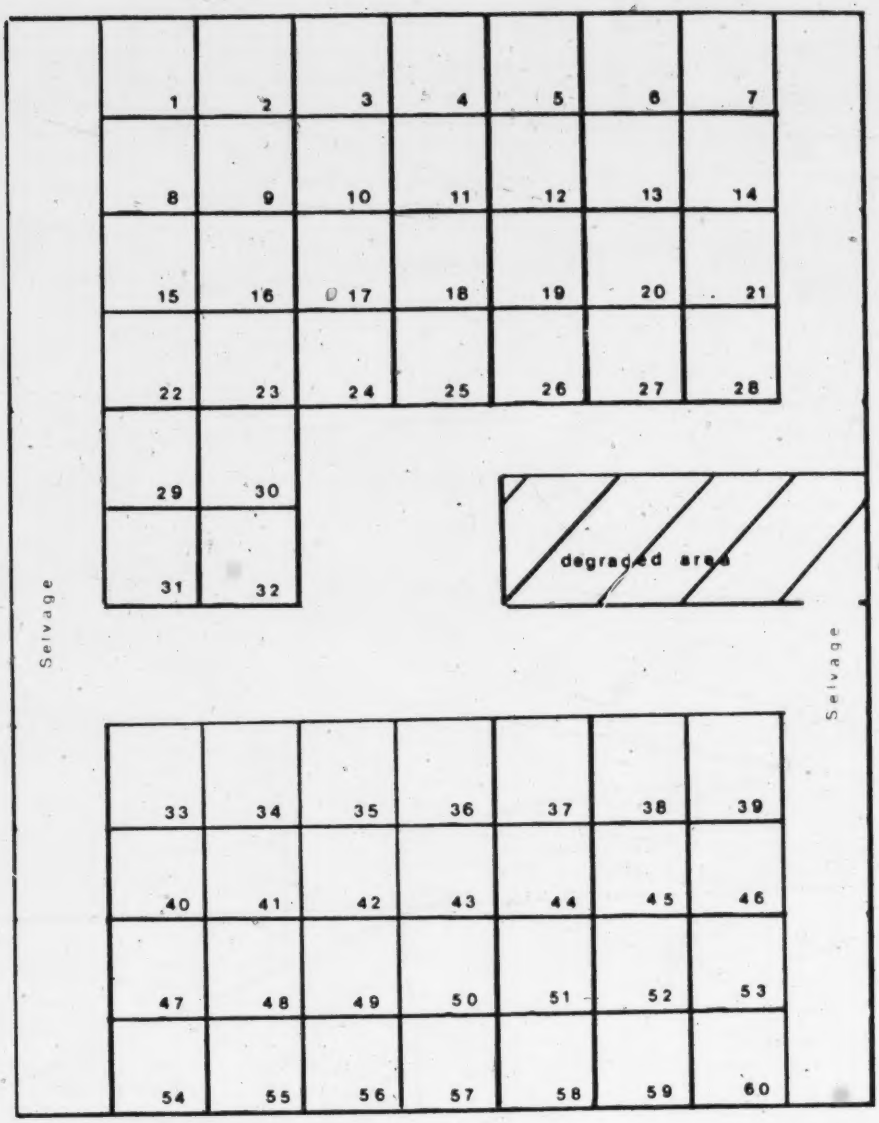
Sampling

Sampling

The fabrics were randomly assigned to each category. Of each category 6 to 7 samples were treated).

Fabric	control	MMMC	$Mg(HCO_3)_2$	$Ca(OH)_2$
A	39	27	22	15
	53	3	24	60
	4	36	33	40
	38	59	2	20
	11	23	43	28
	32	21	8	58
	9	34	35	46
	47	19	7	12
	16	41	54	56
	13	5	57	14
	17	42	10	8
	41	30	48	52
	50	44	51	29
	49	1	6	55
	25	37	26	45
B	2	47	7	1
	41	12	11	58
	39	40	6	28
	49	42	29	31
	19	25	56	26
	54	45	34	20
	10	50	33	24
	5	15	36	57
	17	21	8	35
	38	16	52	30
	27	51	59	48
	37	22	9	32
	23	53	55	43
	14	60	46	4
	3	44	13	18
C	43	10	30	14
	34	38	41	18
	17	5	27	42
	2	25	29	8
	23	4	6	11
	47	45	36	48
	44	21	12	46
	33	31	35	3
	28	7	40	19
	15	22	16	1
	24	13	32	26
	9	20	39	26

D	6	49	44	28
	12	43	35	8
	32	33	25	19
	5	23	10	2
	9	36	3	48
	14	41	11	24
	17	1	20	30
	45	46	7	4
	18	13	42	27
	29	16	37	21
		15	47	34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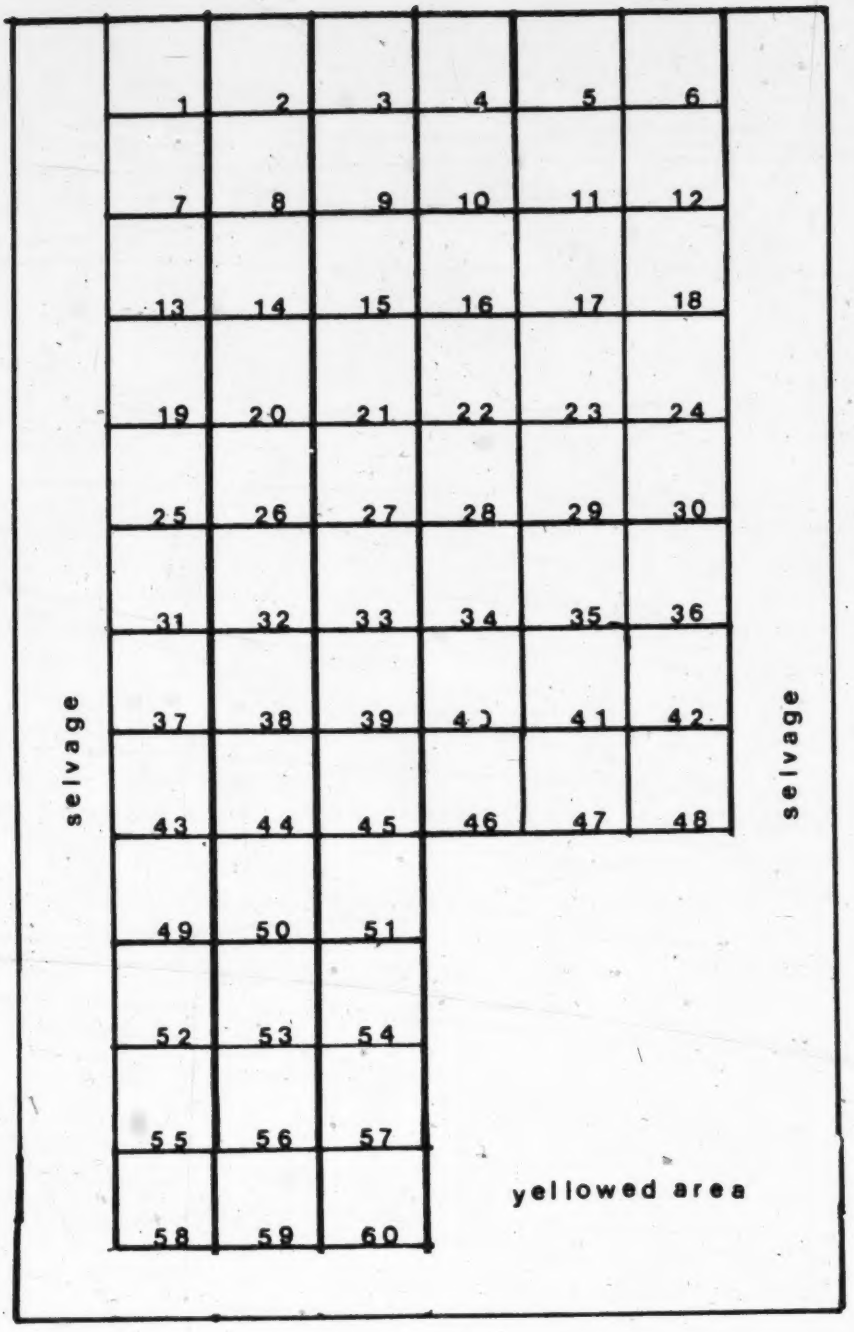
Fabric A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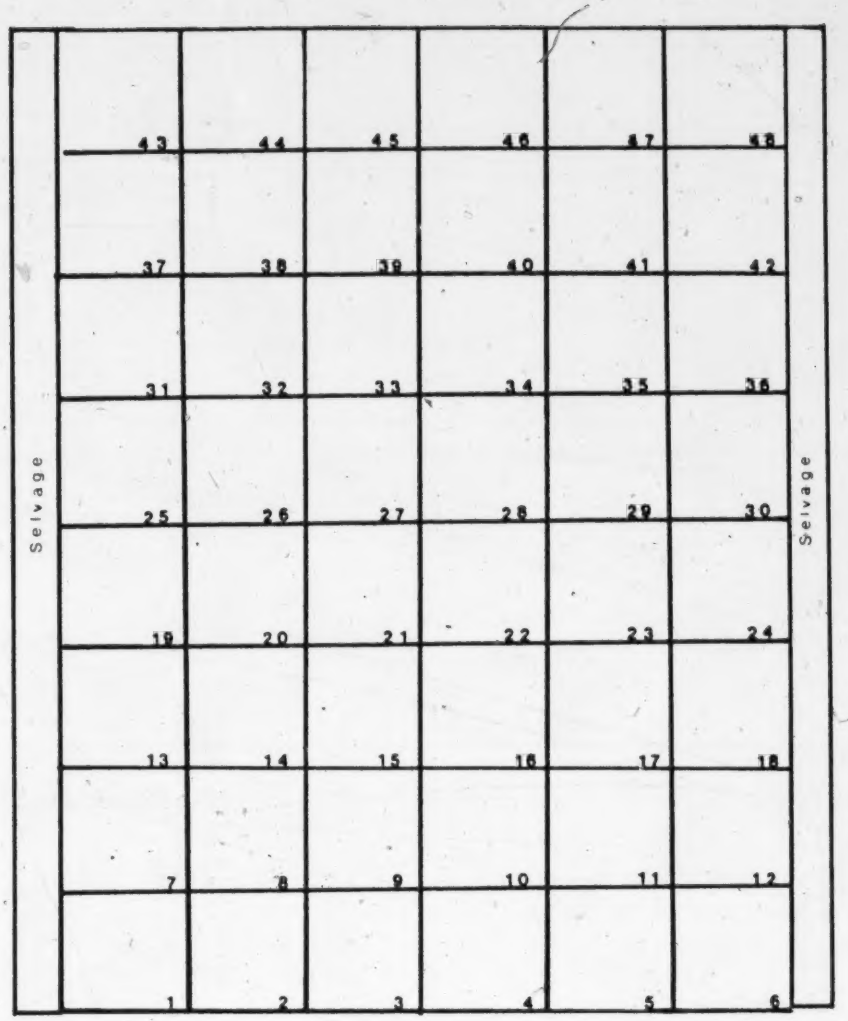
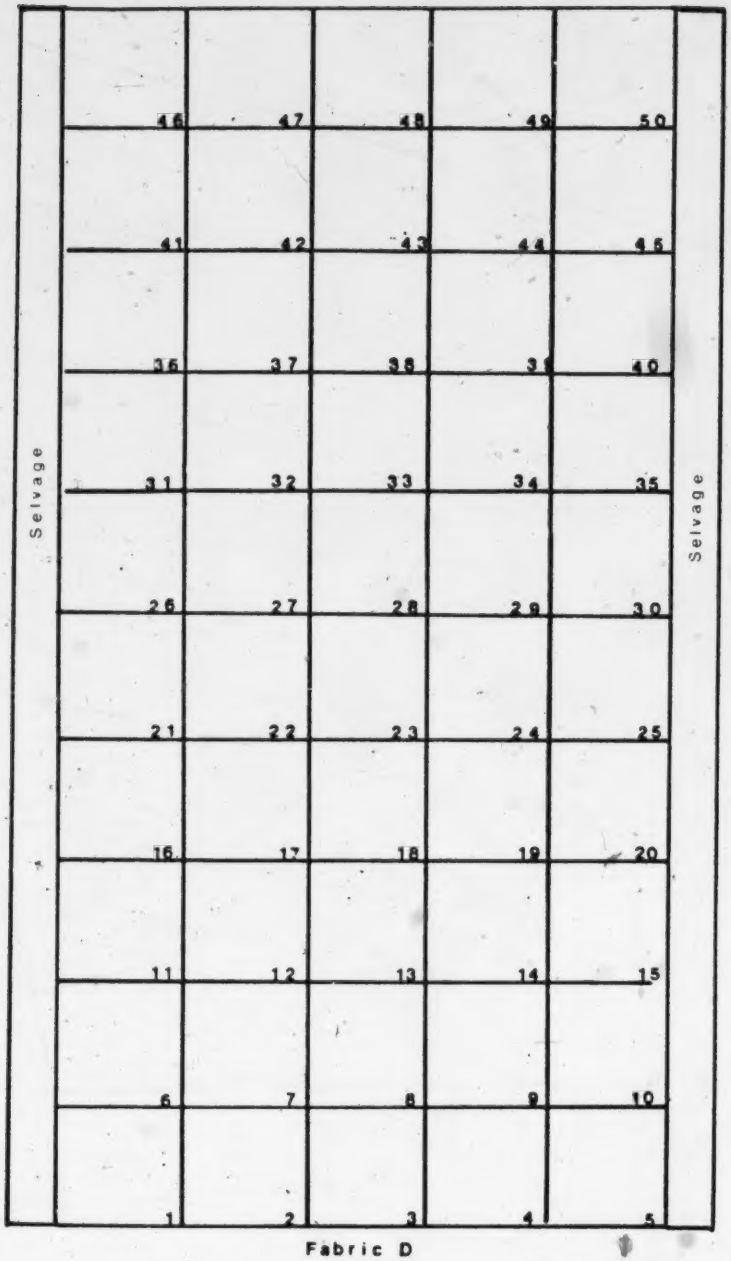
selvage
selvage
yellowed area

Fabric B


Selvage
43 44 45 46 47 48
37 38 39 40 41 42
31 32 33 34 35 36
25 26 27 28 29 30
19 20 21 22 23 24
13 14 15 16 17 18
7 8 9 10 11 12
1 2 3 4 5 6
Selvage

Fabric C


46 47 48 49 50
41 42 43 44 45
36 37 38 39 40
31 32 33 34 35
26 27 28 29 30
21 22 23 24 25
16 17 18 19 20
11 12 13 14 15
6 7 8 9 10
1 2 3 4 5
Selvage
Selvage
Fabric D

Appendix IV

Accelerated aging

Accelerated aging

Fabric	control	MMMC	$Mg(HCO_3)_2$	$Ca(OH)_2$
A	9	14	6	5
	13	20	22	21
	31	28	33	36
	38	45	35	44
	50	56	43	55
		58	57	
B	3	1	9	12
	10	26	11	15
	17	35	34	42
	27	43	46	51
	41	48	59	53
C	2	8	12	7
	24	11	29	20
	28	18	35	22
	34	19	37	31
	47	48	39	45
D	5	2	20	1
	6	4	25	16
	9	819	35	23
	29	19	37	33
	32	28	44	46
		30	47	49
		34		

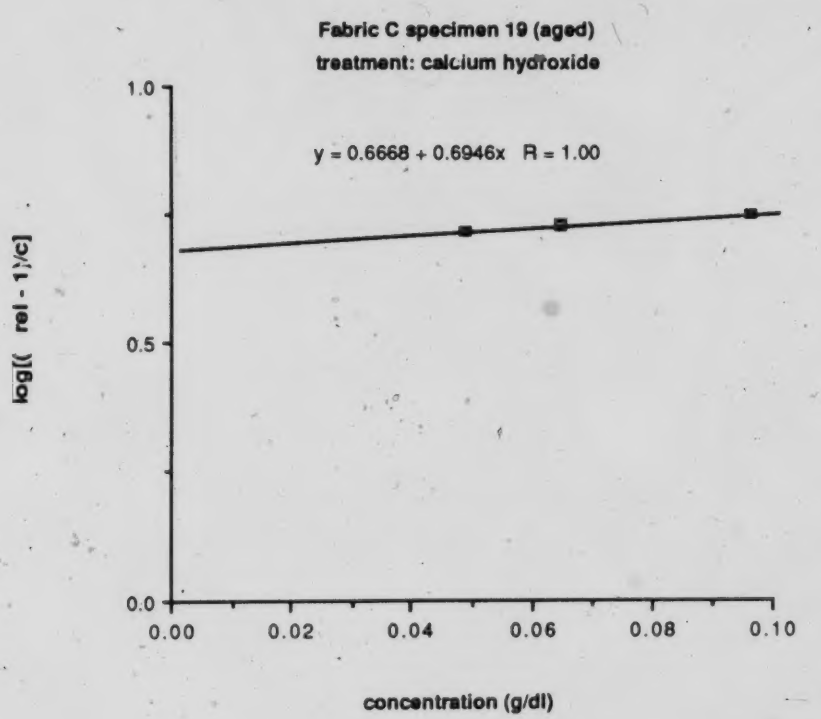
Fabrics which were recapped because of leaking of air during the accelerated aging.

Fabric	control	MMMC	$Mg(HCO_3)_2$	$Ca(OH)_2$
A	55		43	45
				56
B	41			
C	2			18
	28			
D				28
				34

Appendix V

Determination of degree of polymerization: typical measurement

Determination of degree of polymerization: typical measurement



$[\eta rel] = \frac{t}{t_o}$

t = outflow time of solution

t_o = outflow time of solvent (1:1, water cadoxen)

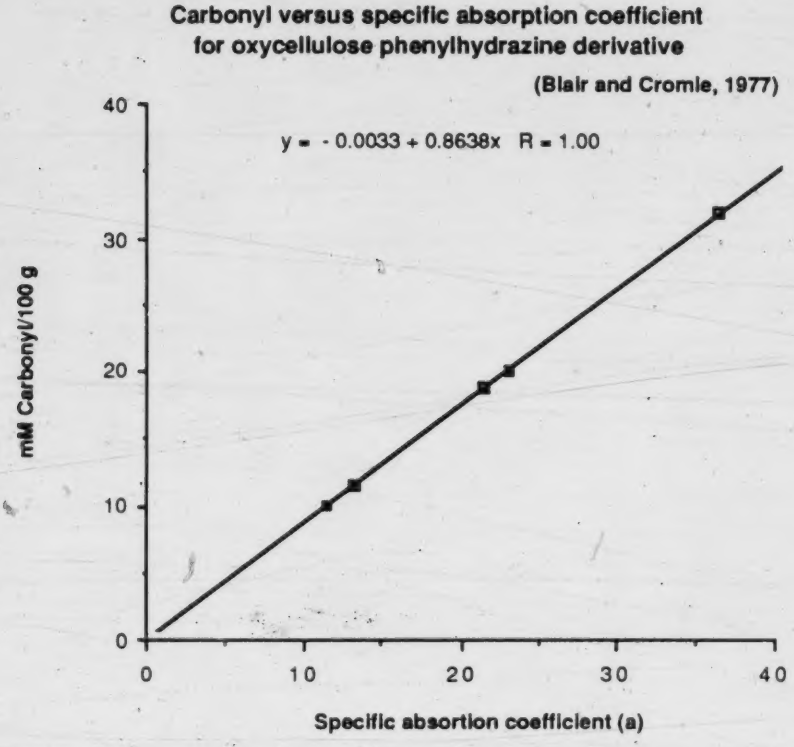
y = log $[\eta rel - 1/c]$ = log [intrinsic viscosity]

$[\eta] = \lim_{c.0} \frac{\eta rel - 1/c}{c \text{ g/dl}}$ = intrinsic viscosity

Appendix VI

Calibration Curve for Carbonyl Determination

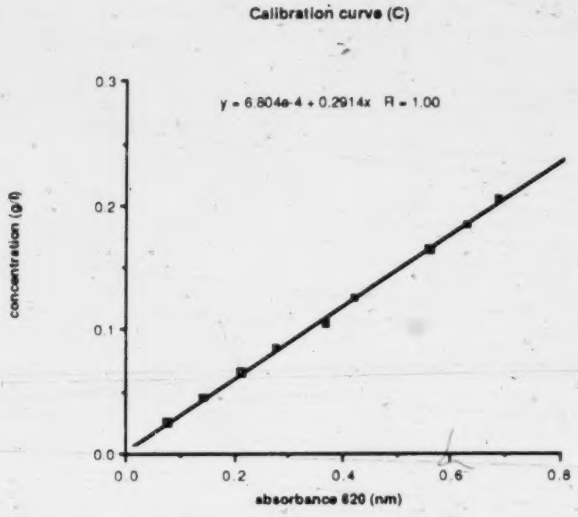
Calibration Curve for Carbonyl Determination.



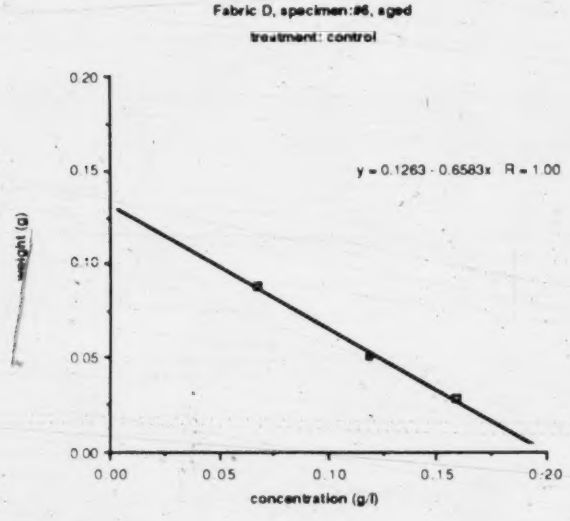
Appendix VII

Calibration curve for determination of carboxyl content and example of calculation

Calibration curve for determination of carboxyl content



Example of calculation



Plot of specimen size versus [Mb^+] (mM/l) from which the mass of cotton which could cause 50% exhaution of the ion concentration was determined; this mass was used in equation XXXIV to calculate carboxyl content.

Appendix VIII

Raw Data

Colour change

treatment	fabric	specimen	ΔE CIELAB units non-aged	aged
control	A	9b[1]	0.0	18.19
		9t[2]	0.0	18.24
		13b	0.0	18.00
		13t	0.0	18.17
		31b	0.0	15.78
		31t	0.0	15.48
		38b	0.0	20.56
		38t	0.0	20.98
		50b	0.0	20.81
		50t	0.0	20.34
	B	3b	0.0	15.83
		3t	0.0	16.08
		10b	0.0	14.99
		10t	0.0	14.75
		17b	0.0	14.87
		17t	0.0	15.08
		27b	0.0	15.60
		27t	0.0	15.54
		41b	0.0	15.67
		41t	0.0	15.40
	C	2b	0.0	26.07
		2t	0.0	25.55
		24b	0.0	20.07
		24t	0.0	19.48
		28b	0.0	19.50
		28t	0.0	19.84
		34b	0.0	20.30
		34t	0.0	20.31
		47b	0.0	19.66
		47t	0.0	20.00
	D	5	0.0	42.05
		2	0.0	42.06
		6b	0.0	41.94
		6t	0.0	41.94
		9b	0.0	42.03
		9t	0.0	42.00
		29b	0.0	41.79
		29t	0.0	42.08
		32b	0.0	46.10
		32t	0.0	46.06
MMMC	A	21b	0.82	17.46
		21t	0.87	17.61

		59b	0.99	10.09
		59t	0.89	10.76
		5b	1.04	17.89
		5t	0.84	18.13
		36b	0.94	19.78
		36t	0.96	19.47
		44b	0.84	19.51
		44t	0.95	19.93
	B	53b	0.62	17.69
		53t	0.66	18.30
		42b	0.76	17.06
		42t	0.92	17.40
		12b	0.74	16.44
		12t	0.84	17.61
		15b	0.51	16.45
		15t	0.57	16.43
		51b	0.69	17.00
		51t	0.37	17.90
	C	7b	1.16	19.72
		7t	1.21	19.49
		45b	0.89	16.34
		45t	1.05	18.53
		20b	0.98	17.81
		20t	1.04	18.65
		31b	1.05	18.14
		31t	1.20	18.94
		22b	1.40	19.09
		22t	1.07	19.74
	D	49b	5.55	36.07
		49t	5.34	37.30
		41b	5.50	32.71
		41t	5.67	33.38
		16	5.28	35.27
		46b	5.57	36.11
		46t	5.52	37.37
		1b	5.46	35.54
		33b	5.57	35.65
		23b	5.81	35.01
$Mg(HCO_3)_2$	A	35	0.42	11.96
		33b	0.41	15.08
		33t	0.77	15.32
		57b	0.36	14.73
		57t	0.40	15.04
		43b	0.41	17.67
		43t	0.45	17.65
		6b	0.26	12.19
		6t	0.29	12.77
		22	0.59	11.07
	B	46b	0.27	13.97

		46t	0.25	13.59
		11b	0.28	13.55
		11t	0.34	14.11
		9b	0.12	15.21
		9t	0.25	16.02
		59b	0.23	14.17
		59t	0.55	13.66
		34b	0.21	13.59
		34t	0.21	13.45
	C	35b	0.39	17.11
		35t	0.33	17.73
		29b	0.32	18.84
		29t	0.30	19.19
		39b	0.36	17.18
		39t	0.31	17.86
		12b	0.35	17.49
		12t	0.28	17.33
		37b	0.34	16.63
		37t	0.27	16.71
	D	47b	7.49	35.00
		47t	7.42	34.77
		42b	7.36	33.29
		42t	7.27	34.39
		25	7.50	33.53
		20	7.56	33.37
		35	7.47	34.84
		37b	7.24	33.20
		37t	7.23	33.39
		44	7.05	33.58
Ca(OH)2	A	45b	0.76	15.33
		45t	0.90	14.20
		58b	0.71	9.98
		58t	0.63	9.99
		56b	0.41	13.51
		56t	0.51	14.78
		20b	0.24	14.67
		20t	0.30	14.63
		28b	0.50	10.88
		14t	0.46	11.34
	B	43b	0.59	16.06
		43t	0.65	16.70
		26b	0.45	16.71
		26t	0.34	16.82
		1b	0.57	15.91
		1t	0.63	16.01
		48b	0.62	15.45
		48t	0.77	15.82
		35b	0.35	15.67
		35t	0.41	16.03

C	19b	0.39	16.84
	19t	0.48	17.26
	48b	0.49	16.26
	48t	0.47	16.03
	8b	0.54	21.35
	8t	0.48	21.23
	18b	0.35	17.94
	18t	0.38	17.44
	11b	0.55	19.61
	11t	0.48	19.79
D	34b	7.54	34.59
	34t	7.30	34.98
	28b	7.31	34.63
	28t	7.14	34.90
	30b	7.84	34.02
	30t	8.34	34.01
	8b	7.51	34.08
	8t	7.97	34.09
	4	7.67	32.20
	2	7.88	32.45

[1] b: bottom left
[2] t: top right

Cold aqueous extract pH

treatment	fabric	specimen	aging	pH
Control	A	11	non-aged	6
		32		6.1
		9	aged	5
		13		5.1
	B	49	non-aged	6.1
		23		6
		10	aged	5.3
		27		5.2
	C	44	non-aged	6.3
		15		6.2
		24	aged	4.7
		47		4.7
	D	14	non-aged	5.8
		45		5.9
		9	aged	3.8
		29		3.8
MMMC	A	44	non-aged	10.2
		1		10.2
		5	aged	9
		36		9.1
	B	51	non-aged	10.3
		15		10.3
		12	aged	8.8
		53		9.1
	C	22	non-aged	10.2
		7		10.3
		20	aged	9.1
		45		9.4
	D	16	non-aged	10.3
		23		10.3
		1	aged	7.4
		53		7.5
MG(HCO3)2	A	35	non-aged	10.4
		6		10.3
		33	aged	8.9
		43		8.7
	B	59	non-aged	10.3
		34		10.
		9	aged	8.4
		59		8.2

	C	12	non-aged	10.3
		37		10.4
		29	aged	7.4
		39		7.4
	D	20	non-aged	10.2
		x		10.2
		37	aged	6.6
		42		6.6
Ca(OH)2	A	45	non-aged	9.5
		56		9.5
		14	aged	8.4
		28		8.4
	B	35	non-aged	9.4
		43		9.5
		1	aged	8.4
		26		8.5
	C	11	non-aged	9.4
		19		9.3
		8	aged	7.7
		18		7.9
	D	19	non-aged	9.4
		30		9.4
		8	aged	7.9
		30		7.7

Degree of polymerization (DP)

treatment	fabric	specimens	aging	DP	[η]
Control	A	11	non-aged	3379	8.84
		32		3303	8.69
		9	aged	1090	3.74
		13		1088	3.74
	B	2	non-aged	1545	4.88
		19		1696	5.24
		17	aged	1097	3.76
		27		1267	4.20
	C	15	non-aged	2112	6.19
		43		2769	7.60
		24	aged	661	2.56
		34		696	2.66
	D	14	non-aged	297	1.39
		45		314	1.45
		6	aged	159	0.87
		9		149	0.82
MMMC	A	21	non-aged	3538	9.16
		59		4179	10.40
		44	aged	2049	6.05
		5		1630	5.08
	B	15	non-aged	1424	4.59
		42		1650	5.13
		12	aged	1168	3.95
		42		1301	4.28
	C	31	non-aged	2587	7.22
		45		2895	7.86
		20	aged	1321	4.33
		45		1319	4.33
	D	x	non-aged	310	1.44
		16		272	1.30
		41	aged	222	1.12
		49		252	1.23
MG(HCO3)2	A	6	non-aged	2748	7.56
		35		3163	8.41
		43	aged	1459	4.67
		57		2198	6.38
	B	9	non-aged	1419	4.57
		11		1748	5.36
		9	aged	1126	3.84
		11		1228	4.10

	C	32	non-aged	2389	6.80
		37		2490	7.01
		12	aged	1711	5.27
		39		1455	4.66
	D	23	non-aged	273	1.31
		44		259	1.26
		25	aged	214	1.09
		44		227	1.14
Ca(OH)2	A	14	non-aged	3160	8.41
		28		3538	9.16
		14	aged	2076	6.11
		20		1834	5.56
	B	1	non-aged	1577	4.96
		48		1771	5.41
		1	aged	1445	4.64
		48		1427	4.59
	C	19	non-aged	2937	7.95
		48		2692	7.44
		18	aged	1250	4.15
		19		1447	4.64
	D	2	non-aged	294	1.38
		4		279	1.33
		8	aged	239	1.18
		12		241	1.19

Carbonyl

treatment	fabric	specimens	aging	carbonyl mM/100 g
Control	A	7	non aged	0.1729
		11		0.1935
		32		0.2132
		47		0.113
		9	aged	0.1595
		13		0.1747
		31		0.1945
	B	19	non-aged	0.1187
		23		0.1298
		38		0.1067
		49		0.1136
		3	aged	0.0538
		10		0.0758
		17		0.0533
		27		0.056
	C	9	non-aged	0.2655
		17		0.1997
		23		0.2058
		44		0.2349
		24	aged	0.2538
		28		0.2181
		34		0.2101
		47		0.2584
	D	12	non-aged	2.7869
		14		2.5871
		18		2.6367
		45		2.6293
		5	aged	1.7593
		6		1.6096
		9		1.7054
		29		1.7828
MMMC	A	5	non-aged	0.0938
		21		0.0583
		36		0.0697
		59		0.0572
		5	aged	0.1197
		21		0.0778
		36		0.1061
		44		0.1336
	B	42	non-aged	0.0842
		45		0.0756
		47		0.0894
		51		0.0970
		12	aged	0.0761

		15		0.1164
		42		0.0909
		53		0.1258
	C	7	non-aged	0.1319
		22		0.1250
		31		0.1585
		45		0.1320
		7	aged	0.0963
		20		0.1123
		22		0.1122
		45		0.1118
	D	1	non-aged	2.1581
		16		2.1075
		23		2.1252
		41		2.0791
		16	aged	0.3758
		23		0.3485
		41		0.2550
		49		0.3893
$Mg(HCO_3)_2$	A	6	non-aged	0.1004
		22		0.0656
		33		0.0913
		x		0.1175
		33	aged	0.0858
		35		0.0876
		43		0.0719
		57		0.1025
	B	11	non-aged	0.0662
		34		0.0544
		46		0.0592
		59		0.1084
		9	aged	0.0649
		34		0.0590
		46		0.0804
		59		0.0814
	C	12	non-aged	0.1837
		29		0.1510
		32		0.1887
		35		0.1366
		12	aged	0.1166
		29		0.0832
		35		0.1112
		39		0.0921
	D	20	non-aged	2.1298
		25		2.2258
		35		2.3320
		44		2.2977

		25	aged	0.4311
		37		0.4759
		42		0.4451
		44		0.6129
$Ca(OH)_2$	A	14	non-aged	0.0524
		20		0.0602
		28		0.0637
		45		0.0835
		14	aged	0.1202
		20		0.1498
		28		0.1558
	B	1	non-aged	0.0706
		26		0.0641
		35		0.0953
		48		0.0630
		1	aged	0.1181
		26		0.1174
		35		0.0993
	C	8	non-aged	0.1995
		18		0.1844
		19		0.1676
		8	aged	0.1902
		18		0.1546
		19		0.1358
	D	8	non-aged	1.8138
		19		1.4094
		28		1.5961
		34		1.5435
		2	aged	0.5571
		8		0.5422
		28		0.5164
		30		0.6046

Carboxyl

treatment	fabric	specimen	aging	carboxyl mM/100g
Control	A	7	non aged	1.6434
		11		1.7422
		17		1.5686
		32		1.3976
		47		1.2399
		9	aged	1.2547
		13		1.4577
		38		1.2626
	B	2	non-aged	1.2723
		19		1.1869
		23		1.1567
		38		1.2151
		49		1.1377
		3	aged	1.1318
		40		1.2796
		27		1.158
	C	9	non-aged	2.0855
		15		2.1645
		17		2.4213
		23		2.0921
		44		1.7286
		28	aged	1.4514
		34		1.5564
		47		1.5314
	D	12	non-aged	3.6364
		14		3.5524
		17		3.4364
		18		3.6298
		45		3.4130
		5	aged	2.8777
		6		3.3113
		9		3.2468
MMMC	A	22	non-aged	1.1703
		33		1.2937
		57		1.0965
		5	aged	1.3550
		21		1.1841
		36		1.2870
	B	45	non-aged	0.8822
		47		0.9234
		51		0.9699
		15	aged	1.0510
		42		1.0599
		53		1.0554

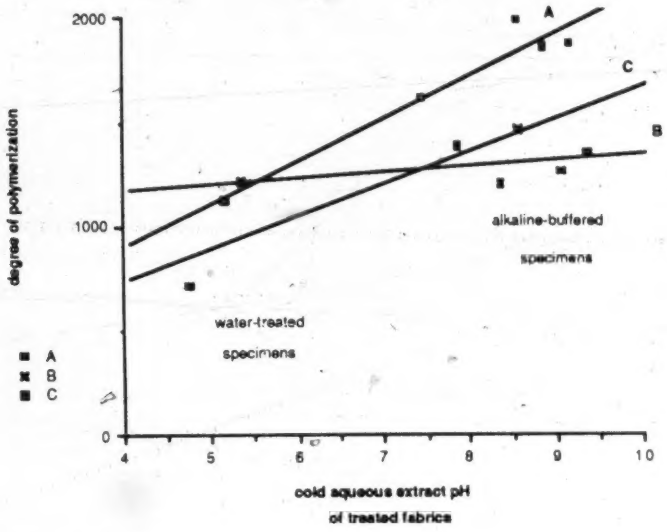
	C	7	non-aged	1.7606
		20		1.4144
		22		1.9861
		31		1.5337
		45		1.3578
		7	aged	1.6807
		22		1.2539
		45		1.5736
	D	x	non-aged	3.3784
		16		3.3167
		23		3.4188
		16	aged	2.6560
		41		2.8571
		49		3.0534
$Mg(HCO_3)_2$	A	22	non-aged	1.2180
		33		1.2330
		57		1.4378
		33	aged	1.0521
		35		1.1905
		57		1.0935
	B	34	non-aged	1.0116
		46		1.0588
		59		1.2353
		34	aged	1.0667
		46		1.2920
		59		1.2399
	C	32	non-aged	1.5540
		35		1.7212
		37		1.6340
		12	aged	1.8100
		29		1.4837
		35		1.6736
	D	20	non-aged	3.7106
		35		3.3445
		44		3.6036
		25	aged	3.8314
		42		3.6364
		44		3.7523
$Ca(OH)_2$	A	20	non-aged	1.3055
		56		1.0805
		58		1.0747
		20	aged	1.0588
		28		0.9221
		45		1.0086
	B	26	non-aged	0.8953

	35		0.8493
	43		0.8673
	26	aged	0.8877
	35		0.8861
	43		0.8913
C	8	non-aged	1.9980
	11		2.0790
	18		1.8100
	19		1.5049
	48		1.3812
	18	aged	1.3784
	19		1.2158
	48		1.1641
D	2	non-aged	3.6101
	4		3.6563
	19		3.6697
	2	aged	2.8490
	8		3.1596
	28		3.1596

Appendix IX

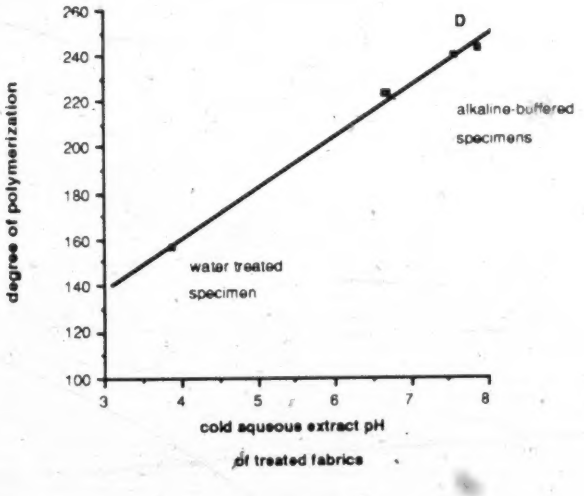
Correlation between tests

Correlation between cold aqueous extraxt pH and degree of polymerization for naturally aged fabrics A,,B and C



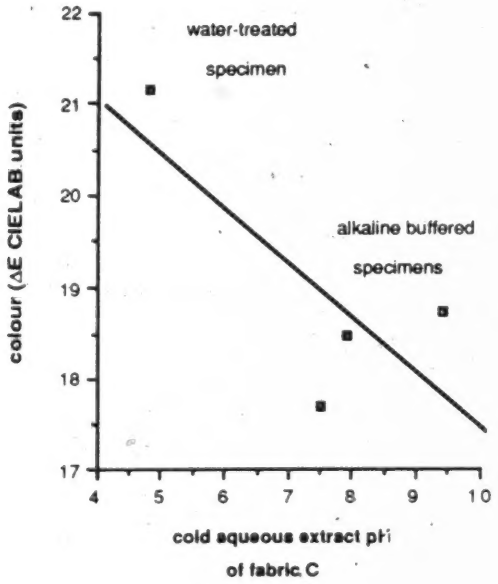
A: R = 0.97
B: R = 0.40
C: R = 0.77

Correletion between cold aqueous extraxt pH and degree of polymerization for artificially aged fabrics

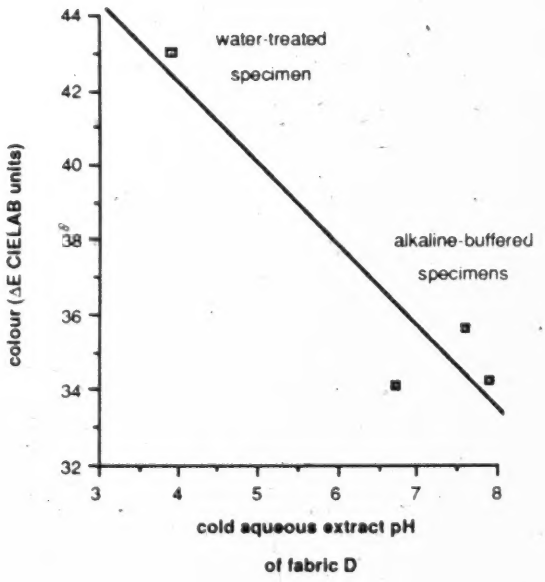


D: R = 1.00

Correlation between cold aqueous extract pH and colour (ΔE CIELAB units) C



C: R = 0.76



D: R = 0.93